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THE ALKALOIDS OF FUMARIACEOUS PLANTS

LI. CORYDALIS SOLIDA (L.) SWARTZ[1]

BY R. H. F. MANSKE

ABSTRACT

Only six alkaloids, namely protopine, allocryptopine, corydaline, *d*-stylopine, *dl*-tetrahydropalmatine, and aurotensine, could be isolated from this plant. The total yield of alkaloids was approximately 0.06%. Chemically, the plant is closely allied with *Corydalis ambigua* and both had been relegated to the same botanical section of the genus.

The section Pes-gallinaceous Irmish of the genus *Corydalis* Vent. includes those representatives in which the root is bulbous and does not become hollow. The best known representative is *C. solida* (L.) Swartz which is widespread throughout temperate Europe. Many minor variations have given rise to an extensive synonomy the most common of which is *C. bulbosa* DC.

It has been examined by Haars (1) who claimed the presence of bulbocapnine and by Heyl (2) who found protopine and two bases melting at 145° and 132° respectively, but has not been further characterized. In the writer's experience this plant is the least rewarding of any in the entire genus. Not only is the total alkaloid content very low (about 0.06%) but only six alkaloids could be definitely identified and these are all known ones, namely protopine, allocryptopine, corydaline, *dl*-tetrahydropalmatine, *d*-stylopine, and aurotensine. These constituents are much the same as those of *C. ambigua* Cham. and Schlecht. (4) and it is perhaps significant that the two plants under discussion belong to the same section.

EXPERIMENTAL

The material for the present investigation was grown in a local garden and the crops collected annually for several successive years. In all cases the aerial portion (7.9 kgm.) was collected at the time the seeds were just approaching maturity. The tubers (6.7 kgm.) were collected at various times of the year. The two portions were worked up separately but no quantitative or qualitative differences were evident.

The procedure for isolating the various alkaloids was the same as that repeatedly used by the writer (3).

[1]*Manuscript received October 3, 1955.*
Contribution from the Dominion Rubber Company Limited Research Laboratories, Guelph, Ontario.

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Protopine and Allocryptopine

The fraction (BS) of nonphenolic alkaloids whose hydrochlorides are insoluble in chloroform was purified by dissolution in dilute acid and regenerating the free bases with ammonia in the presence of a large volume of ether. The residue from the ether extract crystallized readily in contact with methanol and when recrystallized once from chloroform–methanol the resultant protopine melted at 210°C.* either alone or in admixture with an authentic specimen. The small amount of protopine remaining in the methanolic filtrate was separated as its sparingly soluble nitrate and the base then remaining in solution regenerated again by the addition of ammonia in the presence of ether. The residue from the washed ether solution in contact with methanol crystallized at once when innoculated with a crystal of allocryptopine and when recrystallized once from methanol the base melted at 160° either alone or in admixture with authentic allocryptopine. The yield of protopine was *ca.* 0.014% and that of allocryptopine was *ca.* 0.005%. Neither cryptopine nor any further bases could be isolated from the fraction under discussion.

Corydaline

The fraction BC consists of nonphenolic alkaloids whose hydrochlorides are extractable from aqueous solution by means of chloroform. When it was purified by taking through dilute acid and regenerating with ammonia and extracting with ether there was obtained a pale yellow resin which readily crystallized in contact with methanol. The characteristic elongated hexagonal plates thus obtained were recrystallized once from hot methanol and then melted sharply at 135°C. Admixture with *d*-corydaline did not lower the melting point. The yield was *ca.* 0.02%. This is probably Heyl's alkaloid of m.p. 132°.

d-Stylopine

The filtrate from the crystallization of the corydaline deposited a very sparingly soluble base in the course of several days. When it was recrystallized from chloroform–methanol it consisted of colorless prisms which melted sharply at 202°C. either alone or in admixture with *d*-stylopine. The yield was less than 0.002%.

dl-Tetrahydropalmatine

When the mother liquors from the *d*-stylopine were freed of organic solvent and the residue dissolved in hot dilute hydrochloric acid there was formed a sparingly soluble hydrochloride. This was recrystallized from hot water and the base from it recrystallized from methanol. The almost colorless crystals then obtained melted at 150°C. and when they were admixed with *dl*-tetrahydropalmatine there was no alteration in melting point. The yield was about 0.01%. This may be Heyl's alkaloid of m.p. 145°.

Aurotensine

The phenolic fractions (BSE and EES) of the alkaloids whose hydrochlorides are not dissolved by chloroform were combined and converted to

**All melting points are corrected.*

hydrochloride in methanol. The base regenerated from the hydrochloride crystallized in contact with methanol and when recrystallized from the same solvent was obtained in almost colorless rectangular plates which, either alone or in admixture with aurotensine, melted at 128°C. The yield was less than 0.001%.

By reworking other fractions and the mother liquors it was possible to obtain roughly the above yields. It is more than likely that other bases are elaborated by the plant under scrutiny but since the total uncrystallized portion weighed less than one gram there can only be traces of other alkaloids. Bulbocapnine definitely seems to be absent.

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THE POLAROGRAPHY OF THE MONOXIMES AND DIOXIMES OF BENZOQUINONE, NAPHTHOQUINONE, AND ANTHRAQUINONE[1]

By R. M. Elofson[2] and J. G. Atkinson[3]

ABSTRACT

The polarographic behavior of the monoximes and dioximes of 1,4-benzoquinone, 1,4-naphthoquinone, 1,2-naphthoquinone, and 9,10-anthraquinone has been investigated in the pH range 3 to 14. All of the compounds produce well-defined polarographic reduction waves which can be used for analytical purposes. Polarographic evidence indicates that the monoximes and the dioximes exhibit tautomerism.

INTRODUCTION

In this investigation the polarography of the monoximes and dioximes of 1,4-benzoquinone, 1,4-naphthoquinone, 1,2-naphthoquinone, and 9,10-anthraquinone over the pH range 3 to 14 has been studied. Because of the structural relationship of the monoximes with nitroso compounds, the polarography of nitrosobenzene has been reinvestigated.

The polarography of 9,10-anthraquinone monoxime (17), 1,4-benzoquinone monoxime (2), and 1,2-naphthoquinone-1-monoxime (8) has been determined previously and separately over different pH ranges. Recently, Souchay and Ser (15), and Calzolari (5) have reported systematic polarographic investigations of the oximes of aromatic ketones. The oxidation–reduction potential of nitrosobenzene has been previously determined by electromotive force measurements by Lutz and Lytton (10) and by polarographic methods by Holleck and Exner (6). No work has been reported on the polarography of the quinone dioximes.

EXPERIMENTAL

Apparatus

A Leeds and Northrup Electrochemograph Type E was used to record the polarograms. A minimum of damping was employed (position 1) to prevent distortion of the waves.

The capillaries that were used were made from marine barometer tubing obtained from the Corning Glass Works. For the data portrayed in Tables I, II, and IV, the value of h was 54.6 cm., t was 4.13 sec., and m was 2.36 mgm./sec. at zero applied voltage vs. saturated calomel electrode in pH 7 buffer and 50% ethanol at 25° C.

The electrolysis cells were of the usual type. A saturated calomel electrode was used as the anode, connected by means of a flexible saturated potassium chloride agar bridge to the electrolysis cell.

[1]*Manuscript received August 22, 1955.*
Contribution from the Research Council of Alberta, Edmonton, Alberta.
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Media

Buffers were prepared according to Clark and Lubs; pH measurements of alcohol mixtures were recorded with a Beckman Model G pH meter and glass electrode.

Chemicals

1,4-Benzoquinone monoxime, m.p. 136–138° C. (decomp.), and 1,4-benzoquinone dioxime, m.p. 247–248° C. (decomp.), were prepared according to Beilstein.

9,10-Anthraquinone monoxime, m.p. 222–223° C. (decomp.), was prepared according to Julian (7).

9,10-Anthraquinone dioxime was prepared by treating 5 gm. 9,10-anthraquinone with 10 gm. hydroxylamine hydrochloride in 50 ml. of pyridine; the yield was quantitative. Upon recrystallization from methanol it melted at 259–260° C. (decomp.) (11).

1,2-Naphthoquinone-2-monoxime, m.p. 165–167° C. (decomp.), and 1,4-naphthoquinone monoxime, m.p. 190–192° C. (decomp.), were prepared according to Beilstein from α-naphthol.

1,2-Naphthoquinone dioxime, m.p. 150° C. (decomp.), and 1,4-naphthoquinone dioxime, m.p. 221° C. (decomp.), were prepared from the corresponding monoximes by treatment with hydroxylamine hydrochloride and pyridine in alcohol according to Beilstein.

Nitrosobenzene, m.p. 66.5–68° C., was purified by recrystallization from ether.

RESULTS

The Polarography of Nitrosobenzene

In Table I are tabulated the half-wave potentials of nitrosobenzene over the pH range 6 to 11.

TABLE I

HALF-WAVE POTENTIALS OF NITROSOBENZENE VS. S.C.E.
Concentration 0.9×10^{-4} *M* approx.

A. Water solution					
pH	6	7	9	10	
$-E_{\frac{1}{2}}$ volts	0.012	0.075	0.185	0.245	
B. Alcohol 52% by volume					
pH	6.3	8.3	10.4	11.4	0.1 *N* NaOH
$-E_{\frac{1}{2}}$ volts	0.072	0.190	0.320	0.380	0.480

The first series of measurements carried out in aqueous solution obey equation [I]:

$$E_{\frac{1}{2}} \text{ vs. S.C.E.} = +0.339 - 0.0584 \text{ pH}. \qquad [I]$$

This represents the reversible nitrosobenzene–phenylhydroxylamine system whence the normal electrode potential E_0 becomes $0.339+0.246 = 0.585$ v.,

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which is in excellent agreement with the results of Lutz and Lytton (10) who obtained E_0 equal to 0.582 v. by potentiometric titration.

In alcohol solution the relationship between the half-wave potential and the pH as measured with the glass electrode is exactly linear but the equation is given by [II]:

$$E_{\frac{1}{2}} \text{ vs. S.C.E.} = +0.323 - 0.0603 \text{ pH}, \qquad [II]$$

whence E_0 becomes 0.569 volts. The discrepancy in the results, which amounts to about 50 mv. in the actual measurements, is presumably partly due to the errors of measuring pH with the glass electrode in nonaqueous solutions. Similar considerations would probably apply to the other measurements recorded in this paper.

Because of the high volatility of nitrosobenzene exact diffusion current measurements were not made, but the wave heights indicated quite clearly that two electrons were involved in the reduction. This was also evident from a plot of E_{de} vs. log $[i/(i_d - i)]$. Straight lines were obtained with a slope of 27 mv. at pH 7 and 31 mv. at pH 10, which agree well with the theoretical value of 29 mv. for a two-electron reduction.

The Polarography of the Quinone Dioximes

The half-wave potentials of the quinone dioximes in alcohol solution are presented in Table II. All the dioximes were reduced in acid solutions and in strongly alkaline solutions by a process involving six electrons. This was established by comparing the wave heights for anthraquinone dioxime and benzophenone in tetramethylammonium hydroxide solution. Under these

TABLE II

HALF-WAVE POTENTIALS VS. S.C.E. OF QUINONE DIOXIMES
Concentration 1.67×10^{-4} M in 55% ethanol
(minor waves in brackets)

	Dioximes							
	1,4-Benzoquinone		1,4-Naphthoquinone		1,2-Naphthoquinone		9,10-Anthraquinone	
pH	$-E_{\frac{1}{2}}$, volts	n*	$-E_{\frac{1}{2}}$, volts	n*	$-E_{\frac{1}{2}}$, volts	n*	$-E_{\frac{1}{2}}$, volts	n*
3.1	0.09	6	0.13	6	0.07	6	0.37	6
3.9	0.16	6	0.21	6	–	–	0.49	6
5.3	0.30	–	0.34(0.47)	6	0.30	6	0.61	6
6.3	0.39(0.52)	–						
7.3	0.54	–	0.51	6	0.38	6	0.72	6
8.4	0.80	–	–		0.48	–	0.82	6
9.4	(0.79)0.96		(—)0.95	–	0.61(—)	–	0.86(—)	–
10.4	1.10	6	1.01	–	(0.82)1.02	–	(—)1.27	–
11.4					1.05	6	1.32	6
0.1 N NaOH	1.12	6	1.26	6	1.15	6	1.38	6
0.05 M $(CH_3)_4NOH$	1.11	6	1.14	6	1.09	6	1.38	6

**Number of electrons.*

conditions a 2.7×10^{-4} M solution of benzophenone produced a wave of 1.31 μa. and a 0.9×10^{-4} M solution of anthraquinone dioxime produced a

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wave of 1.30 μa. Since the number of electrons required for the polarographic reduction of benzophenone in alkaline solution is known to be two, it follows that the number of electrons required in the reduction of anthraquinone dioxime must be six. The corresponding value for a 0.9×10^{-4} M solution of benzoquinone dioxime was 1.36 μa. under the same conditions. At a pH of 3.1 the diffusion currents of 0.9×10^{-4} M solutions of 1,4-benzoquinone dioxime and 9,10-anthraquinone dioxime in the same concentration of alcohol were respectively 1.32 and 1.26 μa. Therefore it follows that the number of electrons required at the low pH is likewise six. The height of the reduction wave of both of the naphthoquinone dioximes likewise corresponded to the assignment of six-electron reduction waves at low and high pH's.

The surprising equality of the diffusion currents for anthraquinone dioxime and benzoquinone dioxime, despite the fact that the molecular weight of the former was much larger than that of the latter, prompted a controlled potential analysis of anthraquinone dioxime. This was carried out with a 0.001 M solution in 50% ethyl alcohol and buffer of pH 4. A stirred mercury pool was used as cathode and a saturated calomel electrode as anode in order to prevent formation of oxygen. After electrolysis for 12 hr. no cathodic current remained on a test polarogram. Instead, an anodic wave was obtained at -0.20 v. The original cathodic current was 20 μa. The anodic current was 6.5 μa. or almost exactly one-third of the original cathodic wave. Anthrahydroquinone produced an anodic wave under these conditions at about -0.4 v. Since the diamine would have a higher oxidation potential than the anthrahydroquinone, that is, a more positive polarographic oxidation potential, the anodic wave corresponds to the wave of the expected diamine. Further confirmation of this hypothesis resulted when the alcohol was removed under vacuum and a reddish-brown powder was obtained which decomposed at 190° C.; reported m.p. for anthracenediamine 196° C. (14). The powder dissolved in hydrochloric acid and, upon heating, anthraquinone—identified by melting point 270–275° C. with sublimation—was precipitated out (18).

Variation of the height of mercury in the column showed that the height of the reduction waves varied with the square root of h (Table III). This indicates that the waves are diffusion-controlled in both acid and alkaline solutions.

At intermediate pH's the polarograms may show reduction in two steps and the total height of the waves does not correspond to an integral number of electrons. Detailed examination of these waves showed that the lower wave was rate-controlled, while the upper wave was diffusion-controlled, at least when it was the dominant wave. This was proved by the fact that the height of the lower wave was independent of the height of mercury in the reservoir while the height of the upper wave varied with the square root of the height of mercury in the reservoir as shown in Table III.

Kolthoff and Liberti (9) observed similar behavior in the polarographic reduction of N-nitrosophenylhydroxylamine. These authors attributed the kinetic current to the fact that the lower wave corresponded to the reduction of the neutral molecule and the higher wave to reduction of the anion. How-

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TABLE III

EFFECT OF MERCURY HEIGHTS ON REDUCTION WAVES OF QUINONE DIOXIMES
Concentration 0.9×10^{-4} M in 50% ethanol

Dioxime	pH		Current, μa.		Ratio* of current at h_2/h_1
			h_2 = 55.6 cm.	h_1 = 35.6 cm.	
9,10-Anthraquinone	3.1		1.54	1.26	1.22
1,4-Benzoquinone	3.1		1.68	1.32	1.27
1,4-Benzoquinone	10.4	Upper	1.32	1.06	1.25
		Lower	0.38	0.38	1.00
9,10-Anthraquinone	10.4	Upper	1.36	1.12	1.21
		Lower	0.25	0.25	1.00
1,4-Benzoquinone	7.3		0.62	0.62	1.00

*$\sqrt{(h_2/h_1)} = 1.25$.

ever, at the intermediate pH's the concentration of the neutral molecule was calculated to be much smaller than that which corresponded with the height of the reduction wave attributed to it. The height of this wave then corresponded with the rate of formation of the neutral molecule from the anion. Similar behavior has been observed with pyruvic acid and has been attributed by Brdicka (4) to slow formation of the undissociated acid from the anion at the electrode.

However, while the behavior of the quinone dioximes resembles that of these compounds, the kinetic waves cannot arise from the same reason since the dissociation constants are much smaller ($k = 10^{-10}$ to 10^{-12}) than for the compounds just discussed. This fact suggests that isomerization takes place at the electrode at intermediate pH's before reduction occurs. This will be discussed more fully in a subsequent section.

The diffusion currents vary directly with concentration in both acid and alkaline solutions over the concentration range studied of about 0.9 to 1.67×10^{-4} M. At intermediate pH's the waves may be indefinite enough to make quantitative measurement difficult.

The variation of the half-wave potentials with concentration has not been studied in detail. In acid solutions the half-wave potential of anthraquinone dioxime varies markedly with concentration. Changing the concentration from 0.9×10^{-4} M to 1.67×10^{-4} M changes the half-wave potential 0.22 v., whereas with benzoquinone dioxime the variation is much less than 0.01 v. for a similar change. In alkaline solutions the half-wave potentials are independent of concentration.

The Polarography of the Quinone Monoximes

The half-wave potentials of the quinone monoximes at various pH values in 55% ethanol are presented in Table IV. Inspection of the table shows that reduction involves four electrons at all pH values for the four compounds, with the exception of 1,4-benzoquinone monoxime at low pH values and 1,4-naphthoquinone monoxime at pH 10.4 and 11.4. In the latter cases the height of the waves is somewhat smaller than that corresponding to four-electron reductions. Previous workers have reported four-electron reduction for benzoquinone monoxime (2) and anthraquinone monoxime (17).

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TABLE IV

HALF-WAVE POTENTIALS VS. S.C.E. OF QUINONE MONOXIME
Concentration 1.67×10^{-4} M in 55% ethanol
(minor waves in brackets)

	Monoximes									
	1,4-Benzoquinone			1,4-Naphthoquinone			1,2-Naphthoquinone		9,10-Anthraquinone	
pH	$-E_{\frac{1}{2}}$, volts		n*	$-E_{\frac{1}{2}}$, volts		n*	$-E_{\frac{1}{2}}$, volts	n*	$-E_{\frac{1}{2}}$, volts	n*
3.1	–		–	–		–	0.02	4	0.23	4
3.9	0.04		–	0.13		4	0.05	4	0.29	4
5.3	0.14		–	0.25		4	0.16	4	0.38	4
7.3	0.24		(4)	0.31		4	0.23	4	0.48	4
8.4	0.31		4	0.35		4	–	–	0.59	4
9.4	0.46	0.63	4	0.41		4	0.35	4	0.58	4
10.4	( )	0.90	4	0.56	0.75	–	–	–	0.63	4
11.4	0.88		4	( )	0.81	–	0.55	4	0.68	4
0.1 N NaOH	0.82		4	0.88		4	0.65 & 0.78	4	0.91	4

Number of electrons.

The fact that four electrons are involved in the reductions was established not only by comparison with the dioximes but by comparison with *p*-nitrophenol, the polarography of which has been elucidated by Astle and McConnell (2) and by Stocesova (16). In 0.1 N NaOH and 50% ethanol the current due to *p*-nitrophenol at a concentration of 0.9×10^{-4} M was 1.48 μa. and to benzoquinone monoxime at the same concentration was 1.0 μa. Since the reduction of *p*-nitrophenol in alkaline solutions involves six electrons, the reduction of the quinone monoxime involves four electrons.

The reduction of the quinone monoximes proceeds in single steps in acid solutions. In alkaline solutions one wave only is obtained except in the case of the monoxime of 1,2-naphthoquinone in which a stepwise reduction occurs. 9,10-Anthraquinone monoxime provides only one reduction wave at all pH's studied. The other compounds show double waves in the pH range 9 to 11.

TABLE V

EFFECT OF MERCURY HEIGHT ON REDUCTION WAVES OF QUINONE MONOXIMES
Concentration 0.9×10^{-4} M in 50% ethanol

Monoxime	pH		Current, μa.		Ratio* of current at h_2/h_1
			h_2 = 5.6 cm.	h_1 = 35.6 cm.	
1,4-Benzoquinone	4.3		1.4	1.3	1.07
1,4-Benzoquinone	9.4	Lower	0.48	0.48	1.00
		Upper	1.4	1.0	1.4
9,10-Anthraquinone	3.1		1.68	1.34	1.25
9,10-Anthraquinone	13.9		1.80	1.36	1.32

*$\sqrt{(h_2/h_1)} = 1.25$.

Since it was observed that only *p*-benzoquinone monoxime showed abnormally small diffusion currents at low pH's, these were investigated further by varying the height of the mercury reservoir as illustrated in Table V. These

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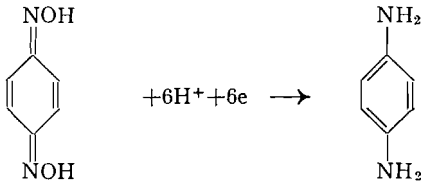
results indicate clearly that the wave at high pH's is diffusion-controlled for both 1,4-benzoquinone monoxime and 9,10-anthraquinone monoxime but only for 9,10-anthraquinone monoxime at low pH's. 1,4-Benzoquinone monoxime at low pH shows a reduction wave which is almost purely kinetic in nature, and this persists to the region where a double wave is observed. This proves that at low pH's the reduction of this compound must be preceded by a change at the surface of the electrode before reduction can take place. Since this reaction could not be the formation of the undissociated acids from the anion (pK for benzoquinone monoxime is about 6), it must involve tautomerization. This may involve the system p-nitrosophenol – benzoquinone monoxime or p-benzoquinone monoxime – p-benzoquinone nitrone.

The diffusion currents have been found to be directly proportional to concentration in the range studied of 0.9 to 1.67 $\times$ 10^{-4} M.

The half-wave potentials were subject to less variation with concentration than was the case with the dioximes. In the case of anthraquinone monoxime at pH 5.3 changing the concentration from 0.9 $\times$ 10^{-4} M to 1.67 $\times$ 10^{-4} M changed the half-wave potential by 0.01 v. In more acid solutions, and also in alkaline solutions, the half-wave potentials were much less dependent or not dependent at all on concentration.

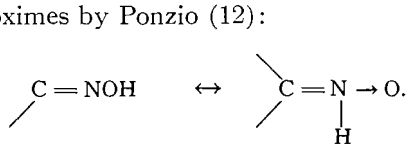
DISCUSSION

The polarographic reduction of the oximes of aromatic ketones (5, 15) has been shown to involve four electrons and results in the production of the corresponding amine. Since the polarographic reduction of the quinone dioximes requires six electrons, the products of the reduction of these substances must be the corresponding diamines, according to equation [III]:



[III]

In the preceding section it has been shown that reduction in neutral solutions is stepwise. Since the lower wave is a kinetic wave, isomerization at the electrode before reduction must be postulated. As it has been pointed out, this must involve tautomerization and not simply re-formation of the undissociated oxime from the anion. Presumably this must involve some form of the classical nitrone–oxime isomerization, equation [IV], postulated originally by Angeli (1) and applied to dioximes by Ponzio (12):



[IV]

It is not possible from the results of this study to state which form is actually reduced at the electrode, but it is hoped that a consideration of these results

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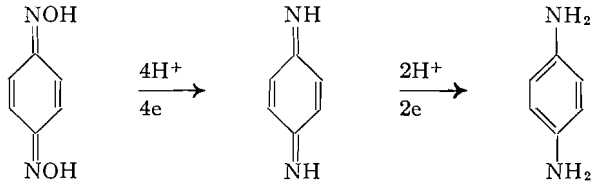
with infrared and ultraviolet spectra analyses currently in progress will elucidate this isomerism. In strongly alkaline solutions, the anion is stabilized by resonance and the molecule is reduced at a considerably higher potential.

The actual reduction probably proceeds according to equation [V]:



[V]

through the intermediate diimino compound. This mechanism is supported by the fact that the slope of the plot of $E_{\frac{1}{2}}$ vs. pH in acid solutions approximates 0.100, which corresponds to a critical step involving four H^+ and presumably four electrons. The results of catalytic and electrolytic reduction of various oximes has necessitated the hypothesis of a similar mechanism. These reductions result in the formation of mixtures of both primary and secondary amines. In order to explain this, von Braun (3) postulated similar imino intermediates which condense with the amine already produced. Elimination of ammonia and further hydrogenation results in the formation of the secondary amine according to equation [VI]:

$$R_1R_2C{=}NOH \xrightarrow[-H_2O]{H_2} R_1R_2C{=}NH \xrightarrow{H_2} R_1R_2CHNH_2 \qquad [VI]$$

$$\downarrow + R_1R_2CHNH_2$$

$$R_1R_2CH{-}NH{-}CHR_1R_2 \xrightarrow[+H_2]{-NH_3} (R_1R_2CH)_2NH.$$

$$\quad NH_2$$

As illustrated in Table III, the polarographic reduction of benzoquinone dioxime at a pH of 7.3 results in a single wave of about one-half the normal height. Since this is a kinetic wave whose height depends on a rate of isomerization, no conclusion can be drawn, at this pH, about the formation of final reduction products corresponding to the dihydroxylamine or the diimino compound. That is, the small wave height may be due entirely to slow isomerization of the dioxime, and only the normal reduction product—the diamine—may be produced.

In all cases where diffusion-controlled waves were observed the reduction of quinone monoximes involves four electrons; hence the over-all reduction product must be the corresponding aminophenol over the entire pH range. On the other hand, the reduction of nitrosobenzene has been shown to stop at the phenylhydroxylamine stage in the pH range studied here. The polarographic reduction of nitrobenzene proceeds to phenylhydroxylamine in alkaline solution, and to aniline in acid solution. *p*-Nitrophenol is reduced stepwise at

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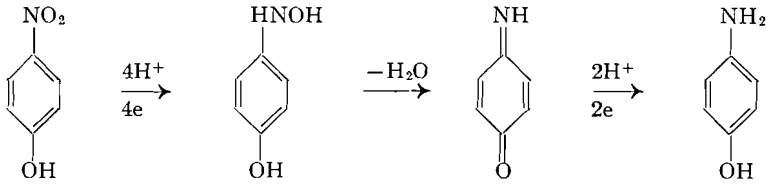
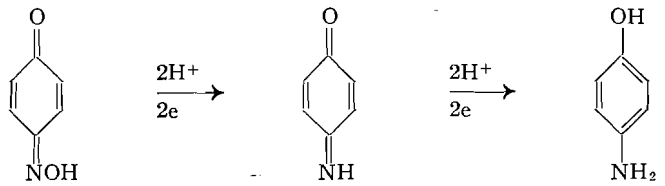
nearly all pH values to *p*-aminophenol. In the case of *p*-nitrophenol these observations have been explained by the hypothesis of quinoidation (16), according to equation [VII]:



[VII]

However, *p*-nitrosophenol (benzoquinone monoxime) is reduced in one step and at more positive potentials than *p*-nitrophenol. For *p*-nitrophenol, at pH 3, Astle and McConnell (2) report a stepwise reduction at $E_{\frac{1}{2}} = -0.41$ and -0.86 v. whereas this investigation has shown a single step reduction at pH 3.9 of $E_{\frac{1}{2}} = 0.04$ v. for benzoquinone monoxime. Furthermore, at pH 12, they found that $E_{\frac{1}{2}}$ was -0.93 v. and -1.57 v. for *p*-nitrophenol, whereas at pH 11.4 this investigation showed $E_{\frac{1}{2}} = -0.88$ v. for benzoquinone monoxime.

These results indicate that the reduction of the monoximes does not involve the intermediate formation of *p*-hydroxylphenylhydroxylamine which would be expected during the reduction of *p*-nitrosophenol, but rather the reduction of the oxime according to equation [VIII]:



[VIII]

This mechanism is supported by the results of the reduction of the quinone dioximes and by the results of the chemical reduction of oximes. The fact that the wave for 1,4-benzoquinone monoxime at low pH's is a kinetic wave indicates that the oxime or other species actually reduced must form slowly at the electrode before reduction can take place. The other monoximes either do not need to rearrange before reduction, or else rearrange very rapidly. As discussed in the section on the dioximes, the possibility of the existence of nitrone forms of the oximes must be considered. This point will require further investigation but the ultraviolet work of Ramart-Lucas (13) confirms the existence of three forms of benzoquinone monoxime in buffered solutions. These are probably nitrosophenol, benzoquinone monoxime, and the corresponding nitrone.

Whereas the reductions of the quinone oximes are irreversible and no particular significance should be placed on the slope of the waves, it is interesting to compare the values obtained by plotting E_{de} vs. log $[i/(i_d - i)]$. In alkaline solution no variation of the slope as a function of structure is obtained, but in acid solution the values obtained for the corresponding monoximes at pH 3.9 are: 1,4-benzoquinone 32 mv.; 1,2-naphthoquinone 52 mv.; 1,4-

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naphthoquinone 58 mv.; and 9,10-anthraquinone 73 mv. The corresponding figures for the dioximes at pH 3.1 are 36 mv., 35 mv., 47 mv., and 69 mv., respectively. The values correspond to actual slopes that are much too low for the number of electrons involved in the reduction. However, it is noteworthy that the derivatives of benzoquinone have much steeper waves than the derivatives of anthraquinone. The derivatives of the two naphthoquinones have waves of intermediate slope. This, of course, is the order of aromaticity of the parent hydrocarbons, the oxidation potentials of the corresponding quinones, and, particularly, the order of conjugation between the functional groups in the oximes themselves.

Since the reactions are highly irreversible, it is not feasible to attach much significance to the actual half-wave potentials of the monoximes and dioximes and their relationship to the reduction potentials of the quinones. However, the fact that the half-wave potentials of the anthraquinone derivatives are at the more negative potentials, and those of benzoquinone derivatives are at more positive potentials, indicates that conjugation is the controlling factor. Since 1,2-naphthoquinone derivatives have potentials very close to those of the benzoquinone oximes, this would indicate a very high degree of conjugation due to proximity of the functional groups.

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THE METAL–SOLUTION SILVER ION EXCHANGE[1]

By I. I. Tingley,[2] I. H. S. Henderson,[3] and C. C. Coffin[4]

ABSTRACT

The exchange of silver ions between silver nitrate solutions and surfaces of metallic silver was studied, using radioactive silver (Ag^{110}, 270 day half-life) as a tracer. Marked differences in behavior of surfaces prepared in different ways were observed. Crystalline (annealed and etched) surfaces exchanged rapidly to a depth of a few atomic layers, and about 80% of the acquired radioactivity was removed as quickly by exchange with inactive silver nitrate solution. Highly polished surfaces exchanged up to ten times as great an extent as the etched annealed surfaces, but required 40 hours' immersion to attain their maximum activity. The deactivation of polished surfaces by inactive solutions was inversely proportional to the period of immersion in active solution, with surfaces immersed for 17 hr. or more retaining all but 30% of their acquired activity. Abraded surfaces exchanged quickly and retained most of their activity, the extent of the exchange depending upon the ratio of "worked" to "unworked" material on the surface. Some evidence of comparatively rapid diffusion in the polish layers was obtained. The interior of cold-worked silver when exposed to the nitrate solution behaved similarly to abraded surfaces. Mechanisms for the behavior of these different types of surface are offered, and the data of other workers discussed.

INTRODUCTION

Experiments on the exchange of silver ions between silver metal surfaces and dilute solutions of silver nitrate were carried out in the Chemistry Department of Dalhousie University between 1948 and 1950. Brief reports on the earlier part of this work have been published (5, 26). While further work is necessary before the exchange mechanisms can be fully elucidated, it was felt that a presentation of these results and suggested mechanisms might be of value to others working in the field.

Excellent reviews of the published work on metal–metal ion exchanges have been made by Haïssinsky (13) and Simnad (23). In order to indicate the development of ideas about the mechanisms, however, a brief summary of certain investigations is given here.

The first published reports of metal–solution ion exchanges are those of Hevesy and Biltz (15). Using lead marked with thorium B, they observed a rapid exchange, extending to 1000 atomic layers, considering the surface to be perfectly flat. They postulated local currents on the surface to account for this exchange, and pointed out that the exchange between a layer of lead dioxide and a lead nitrate solution was much slower. This latter exchange approached much more nearly the ideal case of a "kinetic" exchange, according to their view. A lead sol did not show the rapid exchange with the solution that the massive lead surface did, and the authors explained this as due to the formation of an electrical double layer around each colloidal particle of lead.

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Erbacher was the first to study the effect of surface treatment upon the metal–solution exchange (8). Mechanical abrasion with emery or sandpaper caused on some metals multilayer exchange due to local electrolytic cells, he explained, but with other metals, or after passivation of the cells in certain conditions, only monolayer exchange took place. He also studied similar exchanges between metals and "nobler" metal ions, and used the metallic exchange to measure the actual area of metal surfaces. For silver he found that a polished surface had 1.72 times the area of the surface as measured ordinarily, while coarse- and fine-sandpapered surfaces had 2.49 and 2.53 times the measured areas, respectively.

With abraded silver surfaces (polished with crocus cloth) Rollin observed an exchange involving 150 atomic layers with silver nitrate solution (22). Gold and platinum surfaces also exchanged to a depth of 100 atomic layers with silver nitrate solution.

Cottin and Do Carma Anta carried out experiments with silver metal powder and 0.2 *M* silver nitrate solution. Some of the powder was prepared by chemical reduction of silver nitrate solution by NaH_2PO_2 and some by electrolytic deposition from a 15% silver nitrate solution. The exchange with the metal prepared by electrolysis was found to involve 30 atomic layers compared with 7500 atomic layers for the silver prepared by chemical reduction, in 20 hr. For short times (a few minutes) at 100° C., the exchange involved 20 layers with electrolytic and 1000 atomic layers with chemically reduced silver. The exchange increased with temperature, and decreased after pretreatment with inactive silver nitrate solution. After exchange of long duration, the structure of the powder of chemical origin was found to have modified; it recrystallized in contact with the solution (14).

Simnad and Ruder used radioactive cobalt in solution and surfaces of various metals in both oxygen-containing and oxygen-free solutions (24). They were the first to publish autoradiographs, showing that when an abraded surface was exposed, the radioactive cobalt was deposited on the cathodic (unworked) areas.

Gerischer and Vielstich found a rapid initial exchange which varied in extent with the surface treatment, but was to a depth of 20 atomic layers with crystalline silver. When specimens were immersed for long periods of time, they found a second slower increase in the radioactivity of the metal, and explained this as due to diffusion into the metal lattice. The process was considered to consist of three steps: (*a*) the diffusion through the solution to the surface, (*b*) the discharge of ions at the boundary and their entry into the "exchange-layer", and (*c*) the diffusion into the solid lattice (11).

Baerg and Winkler found that abraded foils, which had 15 times the planar area, as measured by the Bowden–Rideal method, exchanged in one hour to a depth of 30 atomic layers with a 3×10^{-4} *N* silver nitrate solution. When equilibrated with inactive silver nitrate solution of the same concentration for 300 hr. or more, they exchanged with the radioactive solution to a depth of 15 atomic layers. When foils of the same metal were etched with 7 *N* HNO_3, they gave Bowden–Rideal areas of 8 times planar, but exchanged to a depth

of only 2.5 atomic layers, and the exchange was unaffected by inactive equilibration. Fifty to sixty per cent of the acquired radioactivity on both types of surface was subsequently removable by exchange with inactive silver nitrate solution (1).

In kinetic studies on etched surfaces, Baerg and Winkler used the equation $-2.3 \log F = kt$, where $F = (x_3 - x)/x_3$ for the forward equation (inactive surface, radioactive solution) and $F = (x - x_3)/(x_0 - x_3)$ for the reverse reaction (radioactive surface, inactive solution). x is the radioactivity on the surface at time t, x_3 is the value of x at the end of three hours, and x_0 is the initial (zero time) activity for the reverse exchange; k is a proportionality constant. The lines obtained were segmented, with straight portions, except for the reverse exchange from electrodeposited adsorbed ions, which gave a definite curvature. In the earlier portions, the lines for forward and reverse exchanges coincided; after about 12 min., however, the reverse rate was lower, and the slope of its line less. According to the authors, the segmented appearance of the graphs indicates several different rates of reaction and disclosed the heterogeneous character of the metal surface. The curved plot indicated a surface structure of a completely heterogeneous character and suggested random, "out-of-lattice" deposition of the ions. They explained the heterogeneous character of the other surfaces to be due to crystal faces of different orientation, each of which exchanges at a separate rate.

EXPERIMENTAL

A. Apparatus

In the work described below, silver metal surfaces prepared in various ways, as indicated, were exposed to 0.1 N or 0.005 N silver nitrate solutions containing radioactive silver (Ag^{110}, 270-day half life) and to 0.1 N and 0.005 N inactive silver nitrate solutions, with a view to determining the effect of surface treatment upon the exchange taking place between silver metal and its ions in nitrate solution.

The solutions used were as follows:

(1) 0.1 N silver nitrate solution, containing Ag^{110} and giving 4×10^4 c.p.m. per ml. when evaporated on a 1-in. in diameter planchet.

(2) 0.005 N silver nitrate solution containing Ag^{110} and giving 1×10^5 c.p.m. per ml. This solution had a pH of 6.2.

(3) Inactive 0.1 N silver nitrate solution.

(4) Inactive 0.005 N silver nitrate solution, with a pH of 6.2.

The radioactive solutions were prepared by dissolving silver foil of high specific activity in nitric acid and evaporating the solution just to dryness. The resulting silver nitrate crystals were taken up in distilled water, the solution re-evaporated, the crystals redissolved in distilled water and made up to the required volumes. Inactive solution No. 3 was prepared in the same way, using inactive foil, while solution No. 4 was prepared by dissolving Merck

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reagent grade silver nitrate. Isotopic dilution of the radioactive solutions, when necessary, was carried out by the addition of inactive silver nitrate of the same concentration.

The silver metal was obtained from Johnson, Matthey, and Mallory in the form of 0.12 mm. cold-rolled foil and $\frac{3}{4}$ in. in diameter rods. The specimens for the exchange experiments were prepared as $\frac{3}{4}$ in. disks or $\frac{3}{4}$ in. squares of the silver foil, or, in the later experiments, to obtain more reproducible surfaces, 3/16 in. slugs cut from the silver rods. The circular surfaces thus had areas of 2.8 cm.^{2}, and the square ones 3.63 cm.^{2}

Unless otherwise stated, the silver was annealed before each experiment for at least two hours in a muffle furnace at 850° to 950° C. in order to obtain a reproducible starting point for the preparation of each specimen. This annealing produced grains up to 3 mm. in diameter in silver which had been severely cold-worked previously. Surfaces described as "annealed, etched" were prepared by etching specimens of annealed silver with 35% nitric acid, and surfaces described as "emeried" were annealed specimens rubbed with 00 metallographic polishing paper.

Several silver slugs were electrolytically polished. The polishing cell consisted of a 150-ml. beaker containing phosphoric acid (specific gravity 1.7) and a cylindrical silver foil cathode held coaxially with the anode, the slug to be polished. Electrical contact and support for the anode was a 1/16 in. platinum rod threaded into the edge of the slug, and insulated from the solution by a coating of paraffin wax. With a current density of about 50 ma. per sq. cm., electrolytic polishing of the anode took place, producing a bright crystalline surface, with individual crystals well defined in specimens of large grain size.

Silver foil was polished as a strip 6 in. by $1\frac{1}{2}$ in. by hand polishing or on a low-speed polisher, before it was cut into disks or squares. Polishing was carried out by hand using a water suspension of levigated alumina and chamois skin, and on the polisher by affixing the silver strip to a smooth, curved block of wood which was held against a velvet lap continually moistened with a water suspension of levigated alumina. Silver metal slugs were polished by the procedure suggested by Desch (6), using three grades of metallographic polishing paper followed by a smoothing of the surface on a wax lap with levigated alumina. The final polishing was carried out on the low-speed polisher using Linde "B" (alumina) on a "Gamal" lap. The flow of material reported by Beilby (3) in final polishing was observed under a low-power microscope, polishing being discontinued when surface scratches were no longer visible. After polishing, the surfaces were rinsed with water and then with alcohol. In some instances a solution of potassium hydroxide in alcohol was used to remove grease film, followed by distilled water. This treatment had no observable effect on the surface of the metal or on its behavior when exposed to silver nitrate solution.

For exposure to the silver nitrate solution, silver foils were cemented to a picene wax block, and the block suspended in a stirred electrolytic beaker containing 100 ml. of solution. Silver slugs were individually mounted on the

flattened ends of 6 mm. glass rods by means of picene, with the edges of the slugs and the portion of the mounting rods in contact with the solution carefully painted with molten paraffin wax. Seven such specimens mounted on glass rods were exposed to the solution simultaneously, the upper ends of the rods being retained in fuse clips on a circular holder as shown in Fig. 1.

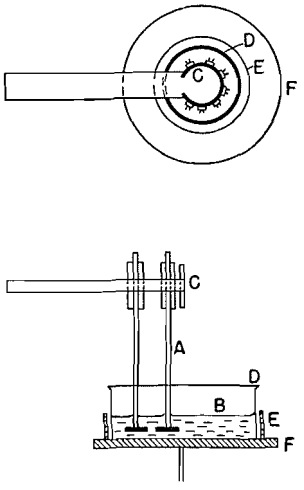

FIG. 1. Slug holder and stirrer assembly. A. Glass rod and silver slug. B. Silver nitrate solution. C. Slug holder with fuse clips. D. 10-cm. crystallizing dish. E. Steel guard ring. F. Phonograph turntable.

It was concluded after runs made both with and without nitrogen bubbling through the solution that the exchange phenomena discussed below were not dependent upon the presence or absence of oxygen. Stirring of the solution at a uniform rate was achieved by revolving the cells containing solution at 78 r.p.m. on a phonograph turntable, the silver specimens being held stationary.

The pH measurements on silver nitrate solutions were made with the system illustrated in Fig. 2, which consisted of a glass electrode, a calomel electrode,

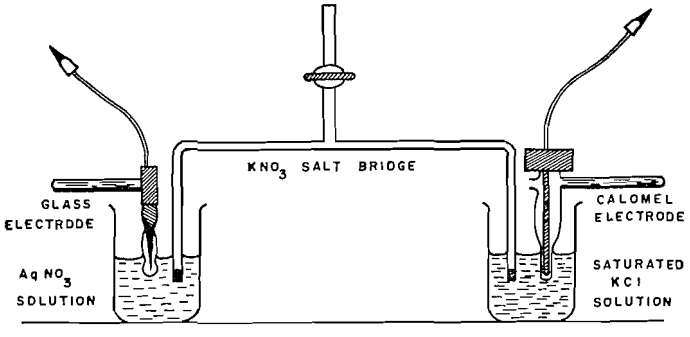

FIG. 2. Apparatus for pH measurement on $AgNO_3$ solutions.

a salt bridge containing 2 *N* potassium nitrate solution, and a Beckman Model G pH meter. The meter was standardized against buffer solution of pH 7.

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After exposure to solution, specimens were rinsed in distilled water, cleaned with boiling benzene and then with detergent (Alconox), and the radioactivity was determined using an end-window β–γ counter in a conventional setup, with the counter tube shielded in a lead "castle". At least 1000 counts were taken from each sample, so the statistical error limit in the counts was 6%. The counts were corrected for day to day fluctuation of the counter efficiency, and for decay, by comparison with a standard Ag^{110} source.

B. Experimental Results

From their behavior toward silver nitrate solutions, the different silver surfaces were classified as crystalline, polished, and "mixed". A "mixed" surface is defined as a surface prepared by scratching, grinding, or partially polishing an annealed specimen, so that some unworked metal is left exposed along with the worked portions.

A number of runs established a marked difference between polished and crystalline (etched) surfaces in the uptake of radioactivity from the solution. Crystalline surfaces acquired very quickly an activity of 10 to 20 c.p.m. from solution No. 1, and this did not increase during immersion up to nearly 90 hr. in the solution, while polished disks acquired radioactivity in a regularly increasing amount until a maximum of about 200 c.p.m. was reached at about 40 hr. After 24 hr. in the solution about 85% of the maximum radioactivity was obtained. Values for a typical run are plotted in Fig. 3.

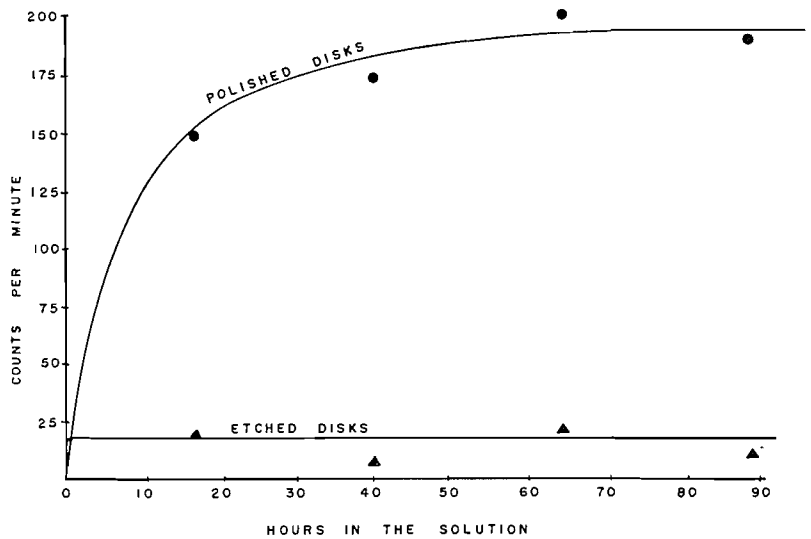

FIG. 3. Activity uptake of etched and polished disks.

Considering the surface of the disks to be perfectly flat, it was calculated that the maximum uptake of radioactivity by the etched and polished surfaces amounted to penetrations of 11 and 110 atomic layers, respectively, i.e., that the amount of silver which had transferred from the solution to the metal surfaces was sufficient to make up these numbers of layers. The value for the

polished surface compared well with the 100 to 150 atomic layers' penetration found by Rollin for silver surfaces, while that for the etched surfaces is comparable to the figures of 20 and 30 atomic layers found by Do Carmo Anta and Cottin for electrodeposited silver, which was certainly crystalline, and to the value of 20 atomic layers found by Gerischer and Vielstich for surfaces etched with nitric acid or electrodeposited from solution.

Using solution No. 2, with a higher specific activity and much lower concentration, a similar pair of curves was obtained, the maximum for the polished surfaces being only five times as high as that for the etched ones, however. There is some uncertainty regarding the number of layers penetrated, due to the fact that the solution radioactivity was determined by evaporating an aliquot on a 1-in.-in-diameter planchet, while the specimens used in the exchange were $\frac{3}{4}$ in. squares. The difference in counting efficiency might be as much as 30%. Neglecting this factor, the penetration with solution No. 2 amounted to only 3.5 atomic layers for etched surfaces and 17 atomic layers for polished surfaces. This value for crystalline surfaces agrees fairly well with those of Baerg and Winkler, who used a solution of 3×10^{-4} N concentration, and would seem to indicate that the depth of the exchange depends to some extent upon the concentration of the solution. Electropolished surfaces prepared from annealed metal without prior abrasion took up approximately the same amount of radioactivity as the etched surfaces, while if the surface was emeried before electropolishing the uptake was two or three times as great.

When the mixed surfaces produced by etching unannealed foil were exposed to the solution along with polished surfaces, the radioactivities acquired by both types of surface were almost identical, as shown by Fig. 4.

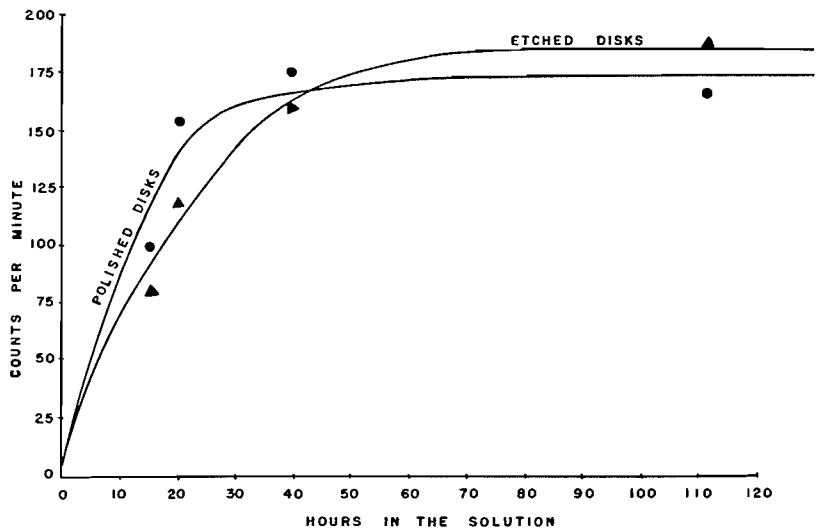

FIG. 4. Activity uptake of unannealed etched and polished disks.

To determine how quickly the radioactivity was acquired upon immersion of the disks in the solution, etched and polished disks were exposed to solution

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No. 1 for instant dips, 10 sec., 1 min., 15 min., 30 min., and 60 min. The results are plotted in Fig. 5. Each count represents a different specimen and

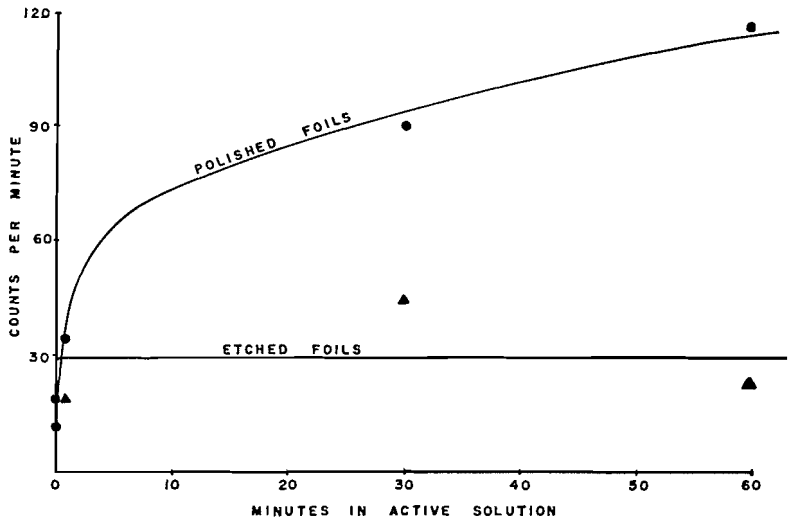

FIG. 5. Behavior of etched and polished surfaces immersed for short periods in silver nitrate solution.

with the etched ones the values were random with respect to time, with the instant dip giving 20 c.p.m. Polished surfaces, though apparently slower starting (13 c.p.m. after an instant dip), continually increased their radioactivity, but at an ever-slower rate, up to the end of the test period.

Experiments with solution No. 2 gave very similar results, to which reference will be made later.

In attempting to show that an electric potential difference existed between the amorphous polish material and the crystalline metal, experiments were carried out in which disks of the same size were connected by a strip of the same foil, the whole dumbbell piece being cut out from a polished strip at one time. One disk of the dumbbell was etched, the other left polished. The piece was placed on the wax block and the connection waxed over, so that the two disks were connected electrically outside the solution. It was thought that if a potential difference existed between the two disks, the polished one would go into solution to some extent, while an equivalent quantity of ions would plate out on the crystalline disk. Compared with unconnected disks in the same solution for the same time, the polished connected disk would acquire less radioactivity and the etched connected one more activity than the respective unconnected ones. The results of many such runs were inconclusive, however, as the effect seemed to be indicated sometimes and in other cases was definitely absent. Modifications on the experimental arrangement were tried, but always the results were inconclusive.

Other workers have observed that the exchange between silver metal and silver ions in solution was diminished by pretreatment of the silver surface

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by exposing it to inactive silver nitrate solution (1, 8, 11, 14), although Haïssinsky and his collaborators found the opposite effect with some metals (14). Polished and etched disks were exposed to inactive solution No. 3 for 19 hr., and then put into radioactive solution No. 1, one pair for an instant, and two other pairs for 30 and 90 min., respectively. The counts obtained on the polished disks were 17, 132, and 168 c.p.m., respectively, while the results for the etched disks were 9, 26, and 36 c.p.m. Later experiments with both foils and slugs in radioactive solution No. 2, after pretreatment for times of 1 min., 5 min., 1 hr., and 17 hr. in inactive solution No. 4, showed that the uptake of activity by both crystalline and polished surfaces was unaffected by pretreatment with inactive solution of nearly neutral pH (6.2). However, using

TABLE I

EFFECT OF ACIDITY OF PRETREATING SOLUTION ON ACTIVITY UPTAKE

Surface	Activity (c.p.m.)	
No pretreatment	100	130 (two disks)
Pretreated with solution of pH 5.4	140	115
Pretreated with solution of pH 0.3	230	250

crystalline silver slugs and inactive 0.005 *N* silver nitrate solution with its pH adjusted, the results found in Table I were obtained after one minute each in the inactive solution and in radioactive solution No. 2. It thus appears that the increase in exchange found with solution No. 1 after pretreatment with solution No. 3 may have been a pH effect. It may also have been just the result of a different degree of polish.

Rollin found that the pretreatment of an inactive silver surface with sodium nitrate solution increased its radioactivity uptake by a factor of 10. When

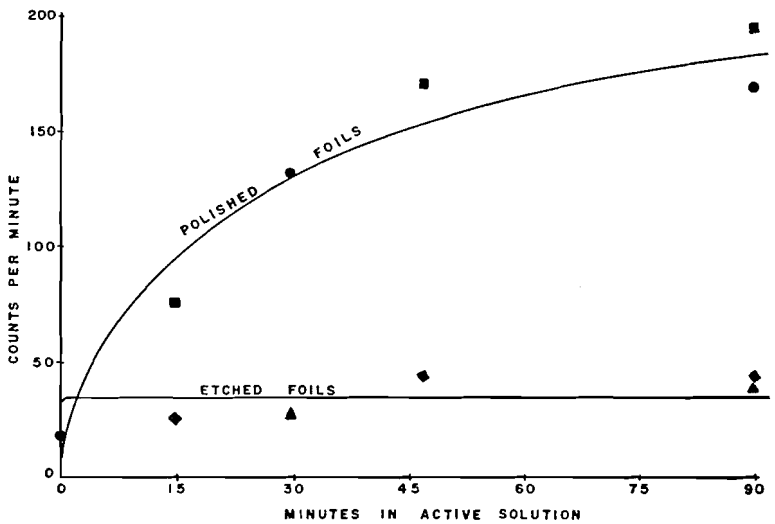

FIG. 6. Effect of pretreatment with inactive solutions upon exchange.

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this was tried by the authors, the results agreed very well with those obtained in the silver nitrate pretreatment, the increase in activity uptake being about 1.5 times for polished surfaces, rather than 10 times, and no change with etched surfaces. More careful experiments should be made to check the effect of pretreatment on the different surfaces. The results of these experiments are plotted in Fig. 6, which should be compared with Fig. 5.

Besides the observation that unannealed foil when etched gave a less obviously crystalline surface, which took up considerable activity from the solution, the effect of cold-working on the properties of the interior of the metal was shown by the following experiments: Two pieces of annealed foil, of the same size, were cut out, and one was pounded with a hammer on an anvil for some time. The two pieces were then set on the wax block, etched, and put into the radioactive solution No. 1. After five hours they were removed and counted. The results were: 98 c.p.m. for the pounded piece, and 17 c.p.m. for the unpounded one. Silver slugs, $\frac{1}{8}$ in. thick, were placed on a steel block and pounded out to a thickness of about 3/64 in. by a single 2000 p.s.i. blow from an electric hammer. After etching with nitric acid, some of these slugs were annealed, and then they were all exposed to the radioactive solution. The unannealed slugs took up three to five times as much radioactivity as the annealed ones.

In an attempt to get a more quantitative idea of the effect of cold working, three pieces of annealed foil, about 2 cm. square, were treated as follows: While it was held between two blocks of wood, the piece was bent through a right angle in each direction for a number of times, and then shifted and bent again at a different place. The pieces were bent in this way at four lines along one dimension, and at four lines along the other dimension, one piece for 4 times, a second for 8 times, and a third for 16 times. (Bending more than 18 times resulted in fracture of the metal.) These pieces were then put on the block along with an unworked piece of the same foil, all four pieces were etched and put into radioactive solution No. 1 for 22 hr. Upon counting, the results were: for the unworked piece, 44 c.p.m.; the one worked 4 times, 56 c.p.m.; 8 times, 53 c.p.m.; and 16 times, 60 c.p.m. Thus, although there was little difference between working the pieces 4 times or 16 times in this way, the difference between worked and unworked appears real. It must be remembered also that etching with the acid undoubtedly removes more of the worked material than the unworked, and so the difference in behavior is probably greater than was found.

To determine how the ratio of "vitreous" or worked metal to crystalline metal affected the uptake of radioactivity, the following experiments were performed.

From a sheet of annealed, etched foil, four disks were prepared, one being polished with wet, fine alumina for 6 sec., a second for 60 sec., a third for 600 sec., and the fourth left unpolished. After being held in the active solution No. 1 for one minute, the disks showed radioactivity as follows: No. 1, (polished 6 sec.) 36 c.p.m.; No. 2 (polished 60 sec.) 111 c.p.m.; No. 3 (polished 600 sec.) 32 c.p.m.; and No. 4 (unpolished) 23 c.p.m. After being in the solution a

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further nine minutes, the disks counted: No. 1, 47 c.p.m.; No. 2, 168 c.p.m.; No. 3, 73 c.p.m.; and No. 4, 28 c.p.m. When returned to the radioactive solution for further periods, the disks increased their radioactivities regularly, with the magnitudes of the increases being in the order No. 2, No. 3, No. 1, and No. 4, until at 17 hours' total exposure to the solution the counts were No. 1, 118 c.p.m.; No. 2, 392 c.p.m.; No. 3, 214 c.p.m.; and No. 4, 67 c.p.m.

When the disks were put into inactive solution No. 3 for the same periods of time, their radioactivities were lost in a similar manner, except that the most highly polished disk retained its radioactivity through the one minute period, while all the others lost considerably. After 17 hr. in the inactive solution the counts were No. 1, 72 c.p.m.; No. 2, 248 c.p.m.; No. 3, 175 c.p.m.; and No. 4, 37 c.p.m.

These results are plotted in Fig. 7.

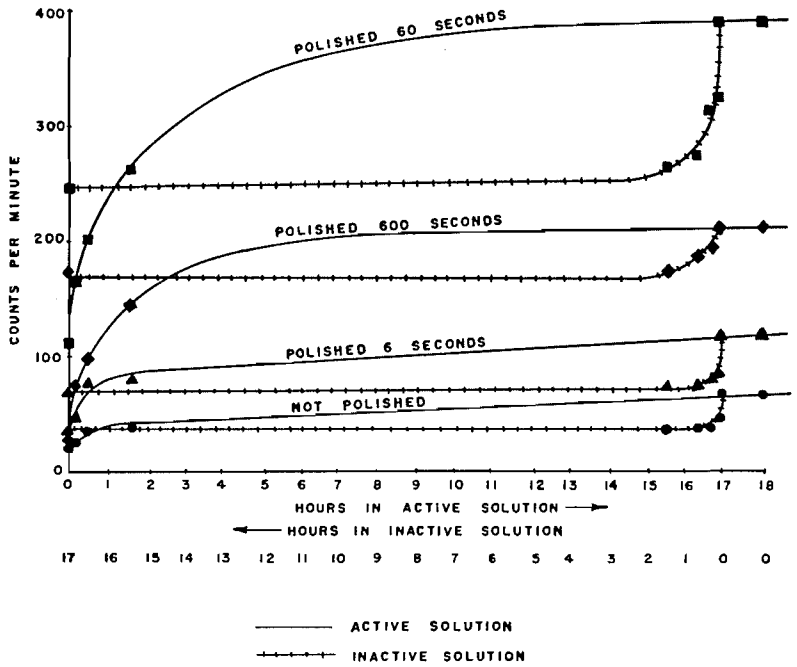

FIG. 7. Effect of vitreous to crystalline ratio upon activity uptake of surfaces.

Two more runs were carried out, in which the numbers of strokes with the polishing chamois were counted, and the foils exposed to solution No. 2 for 17 hr. The results are given in Table II. Another run was made with annealed slugs polished for different times on the Buehler polisher, and the surfaces exposed to solution No. 2 for $17\frac{1}{2}$ hr. The data are given in Table III.

An alternative to the Geiger counter in detecting radioactivity is the method of autoradiography, which has the advantage of indicating the location of the activity more precisely. This would be particularly useful in the case of "mixed" surfaces, it was thought. Autoradiographs of etched specimens of

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TABLE II

Amount of polishing		Activity uptake (c.p.m.)	
1st Run	2nd Run	1st Run	2nd Run
2 strokes	2 strokes	440	1673
4 strokes	21 strokes	846	2100
16 strokes	24 strokes	1520	2760
48 strokes	51 strokes	4170	5400
Good polish	Good polish	3250	4320
High polish	High polish	2870	3985
None	None	240	510
None	None	260	315

TABLE III

Time on polishing lap	Activity uptake (c.p.m.)
None	570
1 sec. (low speed)	1620
5 sec. (low speed)	2430
5 sec. (high speed)	2430
20 sec. (high speed)	2100
50 sec. (high speed)	1910
160 sec. (high speed)	1830

unannealed foil having smooth streaks through the rougher crystalline surface, which had acquired a small amount of radioactivity in active solution No. 1, were made by placing the specimens down on pieces of dental X-ray film, and leaving them in the dark for periods of time necessary to get clear images.

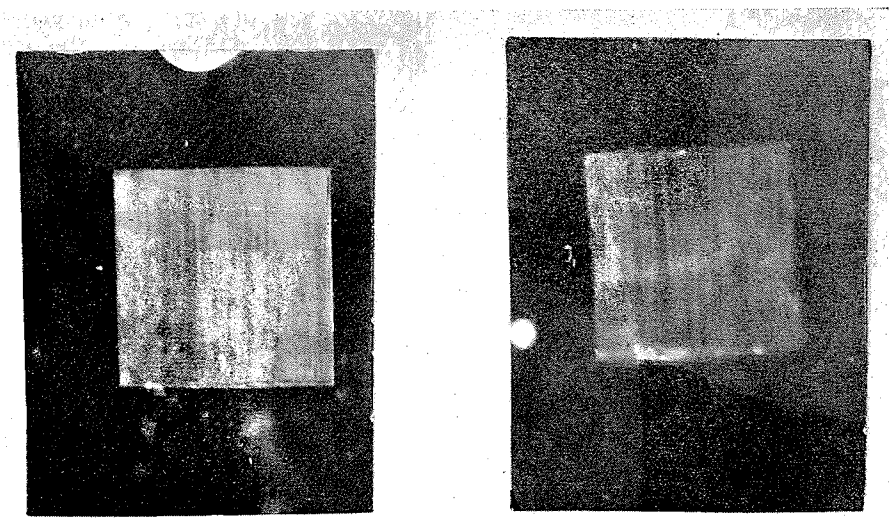

FIG. 8. Photograph and autoradiograph of unannealed etched silver surface. The picture on the left was taken with a camera, with the light placed so that the smooth lustrous streaks were in the shadows of the rougher, more crystalline portions. The autoradiograph, at the right, shows that the radioactivity was concentrated in these crystalline, unworked, cathodic portions of the metal surface.

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When the negatives were developed and compared with the silver surfaces, it was seen that the radioactivity was concentrated on the crystalline (unworked) portions of the surface. This result is similar to that obtained by Simnad and Ruder in their studies with cobalt surfaces and radioactive cobalt solutions (24). Fig. 8 shows a print from the autoradiograph and one from a photograph of the same surface. The smooth streaks were in the shadows of the rougher crystalline portions of the surface when the photograph was taken, and so appear darker in the print. In the autoradiograph they also appear darker, but for the reason that the radioactivity was concentrated on the rougher, crystalline portions, and affected the negative accordingly.

Pieces having surfaces consisting of alternate polished and etched strips were made up, the strips being about 2 mm. wide. These were immersed in radioactive solution No. 1 for several hours, and autoradiographs made of them. These showed that in general the activity was concentrated in the polished strips. However, one etched strip was almost completely active, others were much narrower on the autoradiographs than on the metal pieces, and when the widths of the etched strips on the foils and the widths of the light strips on the films were measured with a micromicrometer, it was found that all light strips on the negatives were narrower than the actual strips on the metal, the differences in width at various positions along the strips varying from 2 to 64%. This was not due to film shrinkage, as the total width of the film image was the same as that of the piece of metal. In these pieces the etched strips were really furrows, being at a lower level than the polished strips, due to the dissolving of the metal during the etching. Considerable radioactivity was probably acquired by the banks of these furrows, since there crystalline metal existed in closest contact with the polish material. Radioactive emanations from these banks would affect the film in such a way that the light streaks corresponding to the etched strips would be narrower than the strips on the metal pieces. This is diagramed in Fig. 9.

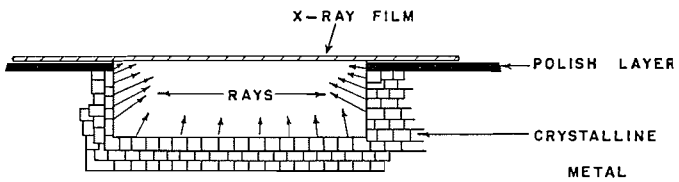

FIG. 9. Diagram of effect of etched and polished strips on film.

The experiments to determine the effect of the ratio of annealed to worked metal indicated that some 20% to 40% of the radioactivity acquired by the silver surfaces after 17 hours' exposure to radioactive solution No. 1 was lost when the surfaces were immersed for an equal period in inactive solution No. 3. The most crystalline surfaces lost the greatest percentage and the most highly polished one the least. Other experiments with well-annealed crystalline surfaces had indicated that such surfaces lost little or none of their acquired radio activity (5), but the low radioactivity taken up made the results highly uncertain. The deactivation phenomena were investigated further, with the more active solution, and the results appear in Table IV.

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TABLE IV

Type of surface	Type of specimen	Time in active solution No. 2	Time in inactive solution No. 4	Per cent loss
Crystalline	Foil	1 sec.	17 hr.	78
		5 sec.	17 hr.	80
		15 sec.	17 hr.	79
		1 min.	17 hr.	86
		17 hr.	17 hr.	75
		1 min.	1 min.	69
	Slug	19 hr.	40 hr.	75
Polished	Foil	1 min.	1 min.	74
		17 hr.	17 hr.	30
	Slug	5 min.	17½ hr.	57
		15 min.	17½ hr.	47
		1 hr.	17½ hr.	60
		4½ hr.	17½ hr.	44
		40 hr.	40 hr.	25
Partially polished	Foil	17 hr.	1 hr.	8
		17 hr.	3 hr.	6
		17 hr.	7 hr.	5
		17 hr.	24 hr.	8
	Slug	17½ hr.	17½ hr.	33
Emeried	Slug	17 hr.	17 hr.	21
		40 hr.	40 hr.	6

These results show that crystalline surfaces rapidly lost from 70% to 90% of the activity they had taken up from radioactive silver nitrate solutions, while polished surfaces which had been in the radioactive solution for at least

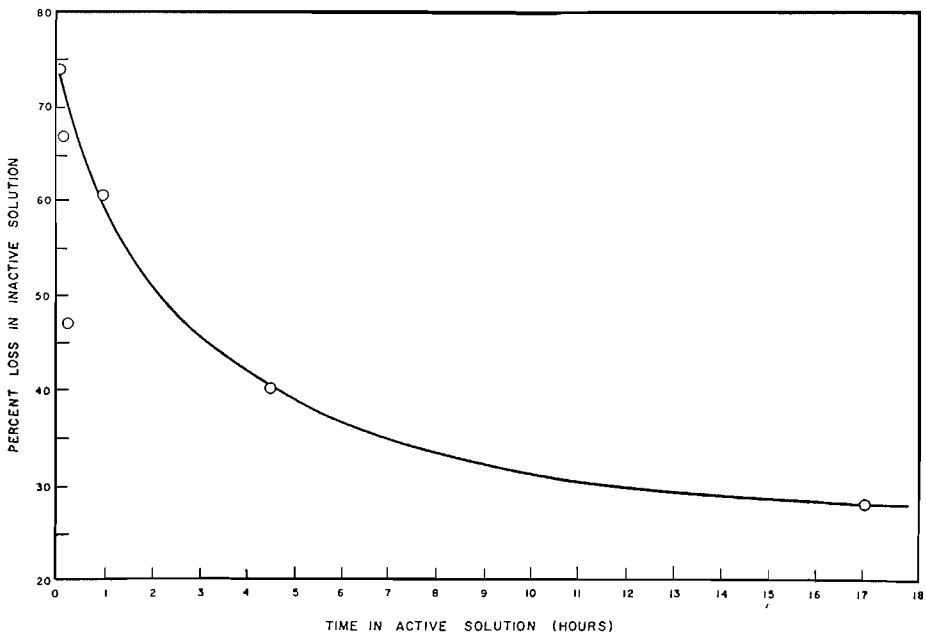

FIG. 10. Relation between deactivation of polished surface and time in active solution.

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17 hr. lost 30% of their radioactivity in inactive silver nitrate solution. The radioactivity lost by polished surfaces in inactive solution was dependent on the time they had been in contact with the radioactive solution. This is shown graphically in Fig. 10. Partially polished foils and emeried surfaces lost the least, 5% to 20%.

The gradual uptake of activity by a polished surface could be nicely explained if atoms which entered the surface layer in the exchange process, including the radioactive atoms by which the exchange was detected, gradually diffused into the polish layer, to be replaced by other atoms both from the metal and from the solution. Diffusion in crystalline silver at room temperature is doubtless very slow (2), but in the disordered, amorphous polish layer it might be thousands of times as rapid as it is along grain boundaries (16). In this way the radioactivity of the metal would increase until the number of radioactive ions entering its surface equalled the number of active atoms re-entering the solution from the surface. In a search for evidence of such diffusion, silver disks which had been activated in an early run were recounted after 228 days. The original radioactivities of two such pieces had been 197 c.p.m. each, and after this lapse of time they counted 92 and 80 c.p.m., respectively, the decrease being accountable by the decay of Ag^{110}. The two disks were immersed in inactive solution for one and one-half hours, which according to previous experiments should have removed 30% of their radioactivity. On counting, however, the results were 97 and 85 c.p.m., respectively, which being within the statistical error limits of the previous counts, indicated that no radioactivity had been lost. To confirm that exchange was still taking place, the two disks were stirred in radioactive solution No. 1 for three hours, whereupon their activities increased to 200 and 210 c.p.m., respectively. Put back into inactive solution for 16 hr., they lost radioactivity to 150 and 148 c.p.m.; returned to the radioactive solution, after 18 hr. they gave 218 and 247 c.p.m.; and after a further 19 hr. in inactive solution 166 and 177 c.p.m. It was apparent that exchange was still going on, but as with new disks, after each exchange period some activity was retained in the foil and could not be removed by exchange with inactive solution.

To see if the original activity had penetrated to the crystalline interior, one of the disks was etched with 4 *N* nitric acid until the polish layer was removed. Upon counting, it gave only 4 c.p.m., which showed that practically all the radioactivity was removed with the polish.

Two more disks of the same age were counted, giving 75 and 77 c.p.m.; these were compared with two disks activated only a short time previously, which had radioactivities of 169 and 176 c.p.m. The old disks were stirred for three hours in inactive solution, and upon counting gave 74 and 78 c.p.m., while the new disks were put for five hours into radioactive solution, after which they gave 244 c.p.m. each. All four disks were then held for 15 sec. in 3.5 *N* nitric acid; no etching of the polish was visible after this. However, after counting, the new disks were seen to have 219 c.p.m. each, and the old ones 70 and 74 c.p.m. The radioactivities found after further periods in the acid are listed in Table V.

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TABLE V

Total time in acid	Old disks (c.p.m.)		New disks (c.p.m.)	
0 sec.	74	78	244	244
15 sec.	70	74	219	219
30 sec.	70	73	218	206
90 sec.	68	63	173	196
450 sec.	38	52	143	162
630 sec.	26	47	87	122

After 450 sec. in the acid, the surface of the polished disks was just beginning to lose its mirror-like finish, while the activities had been cut down 33⅓% to 49% on all disks. It took 90 sec. with the old disks before appreciable removal of activity began, however, while with the new disks effective removal began at once. This would indicate that the penetration of the polish layer by radioactive atoms was only to a small depth for the most part, but that the radioactive atoms diffused into the polish layer with time, so that they were removed from the surface layers where exchange took place.

To determine whether the behavior of the polish layer was changed by heating, pairs of polished foils were heated at temperatures and for times indicated in Table VI before they were placed in solution No. 1 for 17 hr. Micro-

TABLE VI

Duration of heating	Temperature	Activity taken up (c.p.m.)	
None	25° C.	108	110
17 hr.	450° C.	29	76
17 hr.	540° C.	30	25
17 hr.	850° C.	30	25

scopic examination of the above surfaces before activation revealed that crystals were commencing to form in the polished surfaces of all the heated foils, suggesting that annealing of silver can be carried out at quite low temperatures. The data of Table VI confirm this, showing that the heated foils took up radioactivities comparable to those taken up by annealed foils.

Four highly polished silver slugs were heated to 850° C. for different times and then immersed in solution No. 2. After heating, the surfaces of the slugs still had a mirror finish. Table VII shows that heating to 850° C. for short times causes polished surfaces to revert to crystalline behavior with respect to the exchange with silver nitrate solution.

TABLE VII

Duration of heating at 850° C.	Time in solution No. 2	Activity (c.p.m.)
1 min.	17 hr.	1630
5 min.	44 hr.	1020
10 min.	17 hr.	350
45 min.	17 hr.	490

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MISCELLANEOUS EXPERIMENTAL DATA

It was thought that if the polish layer was "vitreous" or, in effect, an undercooled liquid, the behavior of a silver amalgam would be similar. Four polished silver disks were placed on the wax block, and their surfaces amalgamated. The block was immersed in active solution No. 1 for one hour, and then one disk was removed. The disks were all covered with crystals, unevenly deposited, some of which were so loose that they washed off while the block was being rinsed with water. After a further two hours in the solution, a second disk was removed; its surface was as crystalline as if etched with nitric acid. Upon counting, both disks gave more than 9000 c.p.m., and it was concluded that the mercury was displacing silver from the solution.

Two "dumbbell" pieces, or connected pairs of disks, one of each pair polished, the other etched, were put into the same solution that was used in the experiment with the amalgamated disks. One was removed after $17\frac{1}{2}$ hr., and the two disks separated and counted. The etched disk had an activity of 1228 c.p.m., and the polished one 145 c.p.m. After a further $23\frac{1}{2}$ hr., the other pair was removed and counted, the results obtained being 1156 c.p.m. for the etched disk and 257 c.p.m. for the polished. To check this behavior, two more connected pairs and two separated pairs of disks were immersed in the same solution. After two hours, a pair of connected and a pair of unconnected disks were taken off and counted; the results were: etched connected, 101 c.p.m.; polished connected, 39 c.p.m.; etched unconnected, 438 c.p.m.; polished unconnected, 31 c.p.m. After another 20 hr., the remaining pieces showed the following radioactivities: etched connected, 891 c.p.m.; polished connected, 91 c.p.m.; etched unconnected, 649 c.p.m.; polished unconnected, 95 c.p.m. The abnormally high activity taken up by all etched disks, connected or unconnected, since the mercury was put into the solution, indicated that the mercury ions were interfering with the silver ion exchange.

Rollin introduced gold and platinum foils into the radioactive silver nitrate solution, and observed radioactivities taken up by the foils amounting to a penetration of 100 atomic layers. To check this, two gold and two platinum disks were annealed for 24 hr. at 900° C., etched with aqua regia, placed on the wax block, and one of each polished with wet alumina. (The platinum foil was so thin that not much pressure could be used in the polishing.) After immersion in radioactive solution No. 1 for 21 hr., the disks showed the following radioactivities: polished gold, 100 c.p.m.; etched gold, 20 c.p.m.; polished and etched platinum, 10 c.p.m. each. Examined under the microscope, the polished platinum disk showed a very crystalline surface. The counts obtained from the gold pieces seem to indicate that exchange takes place between gold metal and silver ions in silver nitrate solution.

The electrochemical behavior of polished and crystalline substrates of silver was investigated in the following manner: silver from a silver nitrate solution containing Ag^{110} was electroplated on polished and crystalline substrates, and was removed by making the electroplated surface the anode in the plating cell. The electrodes were silver slugs $\frac{3}{4}$ in. in diameter and $\frac{1}{8}$ in. thick. These were supported in the cell by 1/16 in. platinum rods which also served as

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electrical contact with the slugs. The plating bath was 0.002 *N* silver nitrate having a radioactivity of 1.5×10^4 c.p.m. per ml. In these experiments, sufficient silver was plated on the slugs at about 0.3 ma. to give them an activity of approximately 12,000 c.p.m., representing a charge transfer during plating of about 0.09 coulombs. Silver was removed from the slugs by reversing the polarity of the cell and passing about 0.03 coulombs per increment. To determine the amount of silver removed, a coulometer containing the same silver nitrate solution was placed in series with the removal cell, the coulometer cathode and removal cell anode being counted between increments. Activities were corrected for coincidence losses using the manufacturer's statement of the counter resolving time. The coulometer cathode was replaced by an inactive cathode when its activity exceeded 12,000 c.p.m., in order to reduce counting errors. The data are tabulated in Table VIII.

TABLE VIII

Run No.	Substrate type	Anode activity, %	Coulometer cathode activity (as % original anode)
1	Crystalline	100	0
		64.7	29.5
		45.3	54.5
		34.2	81.3
		27.5	103.5
2	Polished	100	0
		95.1	27
		92.8	51
		87.5	99.6
		56.7	161.2
		44.5	228.2
3	Crystalline	100	0
		82.7	24.1
		63.9	71.4
		50.4	133.1
		39.1	200.0
		32.0	269.0
		28.6	330.9
		24.1	424.1
4	Polished	100	0
		94.2	33.5
		88.2	89.3
		82.6	162.8
		80.0	232.3
		77.3	310.7
		74.4	383.4

The curves in Fig. 11, showing activity remaining on the anode plotted against coulometer cathode activity, were made from the data for runs 3 and 4, one employing a polished and the other a crystalline silver substrate. These curves reveal a difference in the behavior of silver electroplated on polished and crystalline substrates, since the silver electroplated on crystalline surfaces was removed much more readily than silver plated on the polished surfaces.

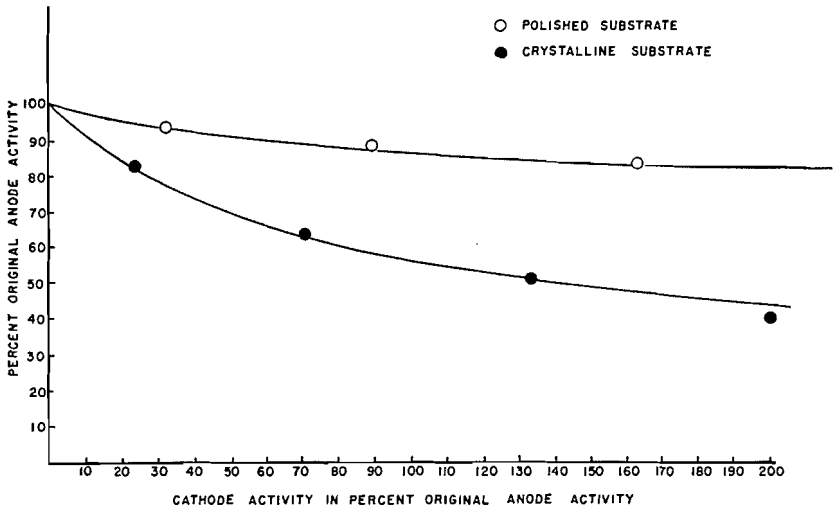

FIG. 11. Electrochemical removal of activity from polished and crystalline surfaces.

DISCUSSION

Of all the work on metal–metal ion exchanges reported to date, the experiments of the present authors seem to be the only ones where care was taken to produce either completely crystalline or completely "non-crystalline" surfaces. As was found in these experiments, etching silver foils in the "as-received" condition sometimes produces surfaces which contain a large percentage of "worked" material. The low extent of the exchanges with etched surfaces found by Baerg and Winkler indicates that the amount of "non-crystalline" material was small; this was merely fortuitous, however. In the experience of the present authors, some foils as received produced good crystalline surfaces when etched with nitric acid; however, the best crystalline surfaces, which take up the least radioactivity from a radioactive silver nitrate solution, can only be consistently produced by annealing the metal before etching.

As far as can be ascertained from the published reports, none of the other workers produced a really good polished surface either. The operation of polishing, as demonstrated years ago by Beilby (3), consists in more than a mere levelling of the surface by wearing down projections. The use of abrasives such as emery results in a cutting down of projections and a working of the surface to some extent, but crystalline metal is left exposed between the scratches made by the abrasive, as can easily be seen with a microscope. The true polishing action is performed only by using a very soft material such as chamois, kidskin, or the felt polishing cloths supplied for use on the Buehler metallographic polishers, and a very fine wet powder (alumina seems to be the best). With the microscope it can be seen that this process causes metal to flow like a liquid for a short distance. Hollows are bridged over or filled in, ridges disappear, and the whole surface becomes very smooth, lustrous, and

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noncrystalline. There seems to be little doubt that the Beilby layer is "vitreous", or, in effect, a supercooled liquid. The local pressures developed must be very high, and it was shown by Bowden and Ridler (4) that the local temperature rises to the melting point of the metal. In electron diffraction studies a pattern similar to that of a liquid was obtained from a polished surface (25), and Finch, Quarrel, and Roebuck discovered that a polished surface of copper dissolved zinc atoms to form a brass, while crystalline copper under the same conditions received only a deposit of zinc metal (9). Dobinski very carefully prepared polished specimens in the absence of oxygen, and showed that the surface was amorphous (7). It is of interest that for silver he found no evidence of oxide on surfaces polished in air. Lees (20) and Hopkins (17) performed experiments which indicated that the polish layer has a depth of 30 Å. For excellent modern ideas about the "Beilby layer" Reference (23) should be consulted (papers other than Simnad's and discussions).

The rapidity of the uptake of radioactivity by crystalline surfaces and the ease of removal of 75% to 90% of it in inactive solution suggests that most of the activity acquired by such surfaces is in the form of an adsorbed layer on the surface. King and Schochet have measured the amount of silver nitrate adsorbed on silver metal powder from solutions, and the results indicate that adsorption amounts to less than one monolayer of atoms (19). A comparable value was found by Baerg and Winkler for activity which seemed to be adsorbed, and could be "plated" onto the surface by rendering the surface cathodic in the Bowden–Rideal cell. The radioactivity which was not removable by exchange with inactive solution was held by Baerg and Winkler to be incorporated into the surface layers of the crystal lattice, and the theories of this crystal growth are well discussed in their papers. Equilibration of the surface for long periods in inactive solution reduced the initial rate of exchange, probably because of the formation of electrical double layers of adsorbed inactive ions, in their view. The present authors suggest it would be expected that exchange with such layers would, if anything, be more rapid than with the crystal lattice, and that the decrease of exchange after equilibration is due to levelling of potential differences on the surfaces, as discussed below in connection with mixed surfaces.

The different behavior of highly polished surfaces indicates a different mechanism for their uptake of radioactivity. That adsorption does take place at first is shown by the deactivation experiments, where it is seen that polished surfaces which had been in the active solution for short times, down to one minute, lost up to 80% of their radioactivity when transferred to inactive solution, and that the radioactivity lost by polished surfaces was dependent on the time they had been in contact with the radioactive solution. After 17 hr. in the solution only about 30% of the acquired radioactivity was removable in this way. The rate of uptake was slower at first—this may be due partly to the smaller surface, and partly to the fact that the lack of a regular lattice makes adsorption more difficult. The regular increase of radioactivity taken up, the longer time required, and the greater retention after equilibrium is reached show that 70% of the silver ions which enter the metal become

unavailable for exchange. This can be due to changing of the surface structure as proposed by Haïssinsky, or to diffusion into the polish layer and thus away from the surface. The changing of the surface structure would presumably result from the dissolution of the anodic polish layer and the plating out of the silver ions from the solution in a crystalline form. This mechanism might explain the phenomena observed in the "controlled exchange" (Table VIII). If the silver plated out in crystalline "trees", on reversal of polarity the less noble polish material would dissolve first, leaving most of the Ag^{110} on the metal surface. Several further experiments might check this mechanism. Silver is notorious for its tendency to plate out as large "trees" from nitrate solutions, but addition agents such as gelatin make more uniform deposition possible. Plating from cyanide solution also results in smooth, uniform deposits. If this mechanism is correct, silver plated on polished substrates from silver nitrate with gelatin or from cyanide solutions should be more readily removed when the current is reversed. Similarly, the exchange between metal surface and solution should be affected if such addition agents or complexing agents are used.

The other explanation of the behavior of highly polished surfaces is that a truly "kinetic" exchange takes place between the polish layer and the solution, analogous to that between a liquid metal like mercury and an aqueous solution of one of its salts. According to this view, silver ions on the polished surface change places with silver ions which strike the surface from the solution. Because of the amorphous or vitreous state of the metal in the polish layer, the atoms or ions in it have a much greater mobility than do those in crystalline metal. Besides enhancing the exchange activity, this increased mobility allows a more rapid diffusion into the interior of the polish layer, and thus a greater extent of radioactivity uptake. The behavior of the foils which had been left for 228 days after their first activation and then did not deactivate at first with inactive solution or even lose activity when etched with dilute acid, although in radioactive solution they rapidly acquired more activity part of which was removed if the foils were again immersed in inactive solution, seems to support the diffusion hypothesis. The dissolution of zinc atoms in the polish layer on copper, reported by Finch, Quarrel, and Roebuck, and the work of Finch and Sun on electroplating onto polished substrates (10) inclines to the view that the behavior of the polished surface is due to actual entry of the ions from the solution into the liquid-like polish layer. It should be possible by further experiments, such as by pretreatment of long duration of polished surfaces in inactive solutions, and by diffusion experiments, to establish one or other of these mechanisms as the correct one.

On mixed surfaces, such as are prepared by exposing the interior of cold-worked metal, or by abrading with emery or partially polishing a crystalline surface, much of the radioactivity would seem to be acquired by electrolytic deposition onto the more crystalline portions, due to the local potential differences between the anodic worked or vitreous areas and the cathodic crystalline portions of the surface. This is shown by the autoradiographs of the surface of the cold-rolled piece, Fig. 8, and those of Simnad and Ruder. On such

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a worked surface the actual area of the metal is much greater than on an annealed surface, owing to fragmentation of the crystallites, and a virtually infinite number of crystal faces with completely random orientations, of both low and high indices, is exposed. This condition greatly enhances the exchange ability of the surface, but in addition there is the electrolytic action between the anodic worked material and the cathodic ordinary crystalline material. When potential differences have been evened out, and the local currents have ceased, exchange between any vitreous material remaining and the solution can still take place, so that the final amount of radioactivity uptake and the distribution of the radioactivity depend upon the relative amounts of worked and unworked metal on the surface. Tables II and III and Fig. 7 show how the ratio of vitreous and crystalline metal affects the rate and extent of activity uptake by the surface. When the vitreous material exceeds a certain proportion the uptake of radioactivity decreases, the surface behaving more like a completely polished one.

Heat treatment of polished surfaces resulted in a revision of their behavior to that of crystalline surfaces, although these surfaces still appeared highly polished after heat treatment. It would be interesting to see whether short heat treatment results in the formation of a mixed surface before truly crystalline behavior begins.

The retention of radioactivity up to 95% by mixed surfaces when transferred to inactive solution supports the belief in the electrolytic deposition mechanism, since ions when plated onto the crystalline metal would not exchange like those merely adsorbed as in the beginning of the ordinary exchange process.

The decrease in activity uptake after long immersion in inactive solution, observed by Baerg and Winkler using abraded foils, can be explained as due to the evening out of local potential differences, so that the electrolytic action does not take place when the surface is exposed to the radioactive solution. The result of the dissolving of anodic material and the deposition onto the crystalline metal should result in the surface becoming more crystalline, or completely crystalline, if the ratio of vitreous to crystalline metal is right. With a perfectly polished surface, however, there should be no electrolytic action, and in the absence of nuclei, no recrystallization, unless nuclei are formed by the action of the solution. Rollin's observation of the effect of sodium nitrate solution on his mirror surface would indicate that the surface was activated in some way by the solution, perhaps by the formation of an absorbed double layer of sodium and nitrate ions, which exchanged rapidly with the silver nitrate solution.

The exchange with gold and platinum surfaces must be due to either adsorption, intermetallic compound formation, or a purely kinetic exchange, resulting in the formation of a solid solution, as observed by Finch *et al.* with zinc and copper. These metals are too far below silver in the electrochemical series for any electrolytic action between them. The exchange experiments with the silver amalgam, on the other hand, seem to show much electrolytic action between mercury (with a standard potential of -0.7986 v.) and vitreous and crystalline silver. (The standard potential of silver is given variously in

tables as −0.7978 v. and −0.7995 v.) Rapid kinetic exchange between mercury and silver nitrate solution probably took place also, and perhaps initiated the electrolytic action, by allowing the mercurous ions to get into the solution. It would appear that the vitreous silver displaced mercury ions from the solution, which in turn displaced silver ions onto the crystalline silver metal. The papers of Groh (12) and Kayas (18) should be consulted for the behavior of amalgams other than silver.

The exchanges with polished and mixed surfaces all follow fairly satisfactorily the empirical equation $\log x = a \log t + b$, first stated by Haïssinsky (where x is the radioactivity of the metal, t is the time of immersion, and a and b are constants which differ for each run), until a maximum value is reached, when the curve levels off. The data for the highly polished surfaces also may be expressed by the equation $\log[(x_\infty - x)/x_\infty] = kt$, where x_∞ is the

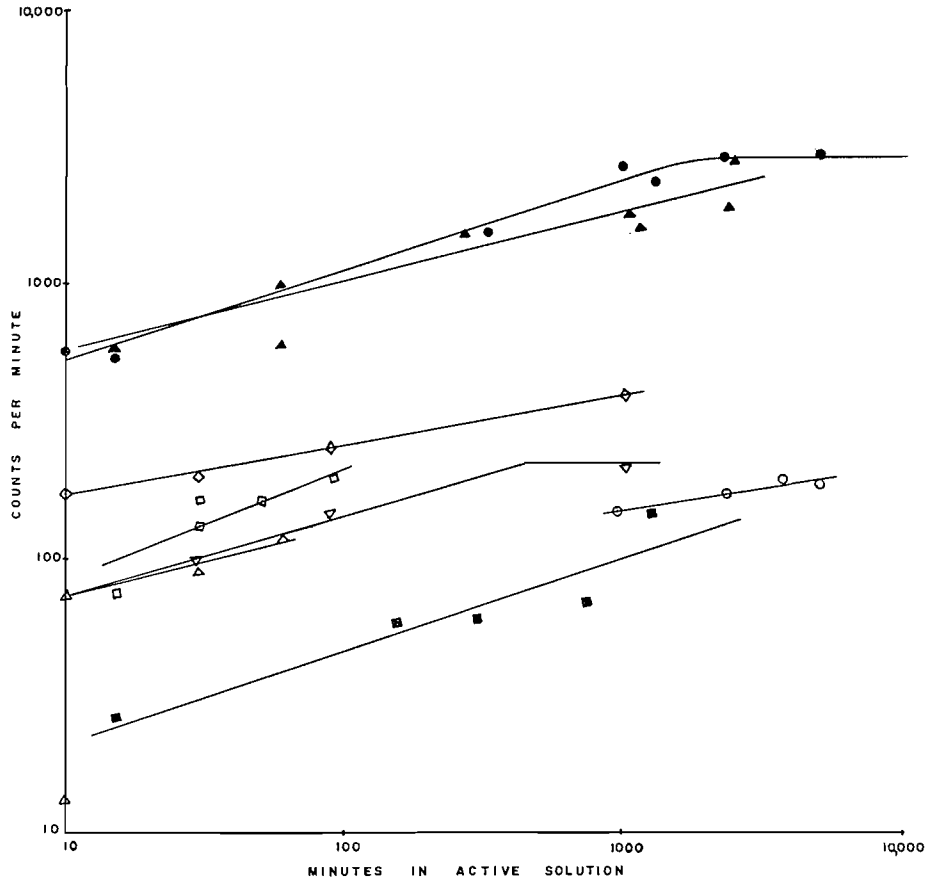

FIG. 12. The uptake of activity with time, according to the equation of Haïssinsky, $\log x = a \log t + b$.

○ Data from Fig. 3
△ Data from Fig. 5
□ Data from Fig. 6
◇ Data from Fig. 7 (Abraded Foils)
▽ Data from Fig. 7 (Polished Foils)
● Data from run with solution No. 2
■ Data from run with solution No. 1
▲ Data from run with solution No. 2

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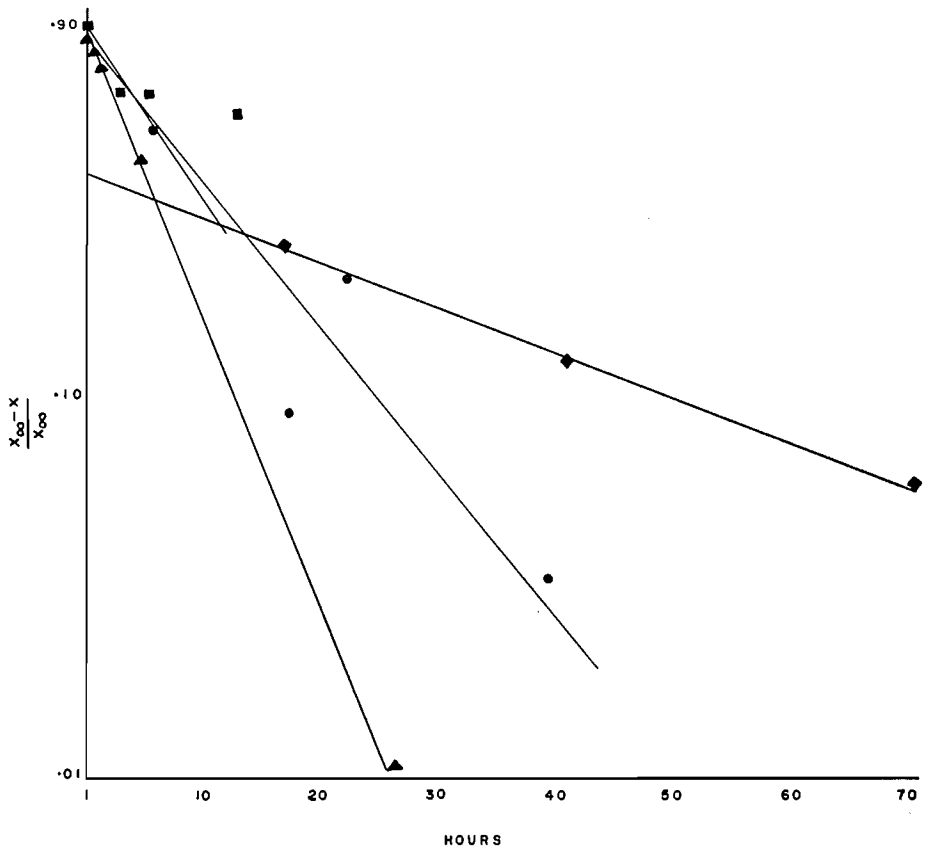

FIG. 13. The uptake of activity with time, according to the equation $\log[(x_\infty - x)/x_\infty] = kt$.
● Data from run with solution No. 2
■ Data from run with solution No. 1
▲ Data from run with solution No. 2
◆ Data from Fig. 3

maximum radioactivity taken up, and x is the radioactivity at time t. This latter equation is the one followed by mercury and amalgams, as well as by silver metal powder and copper, and indicates a kinetic type of exchange. The reverse exchange (radioactive metal – inactive solution) for a mixed surface also follows the equation of Haïssinsky (with different values for the constants), but that for a highly polished surface fitted the equation $\log x = at + b$ rather better. This of course is also a first order kinetic equation, being the integrated form of the equation $dx/dt = ax$, and indicates that the concentration of radioactive atoms, x, available at the beginning of the exchange remains so during the measurements. The differential form of Haïssinsky's equation, $dx/dt = ax/t$, shows that the rate of change of activity in the metal is inversely proportional to the time, as well as being directly proportional to the initial concentration. This seems to indicate that the number of active atoms at the surface available for exchange becomes smaller in a

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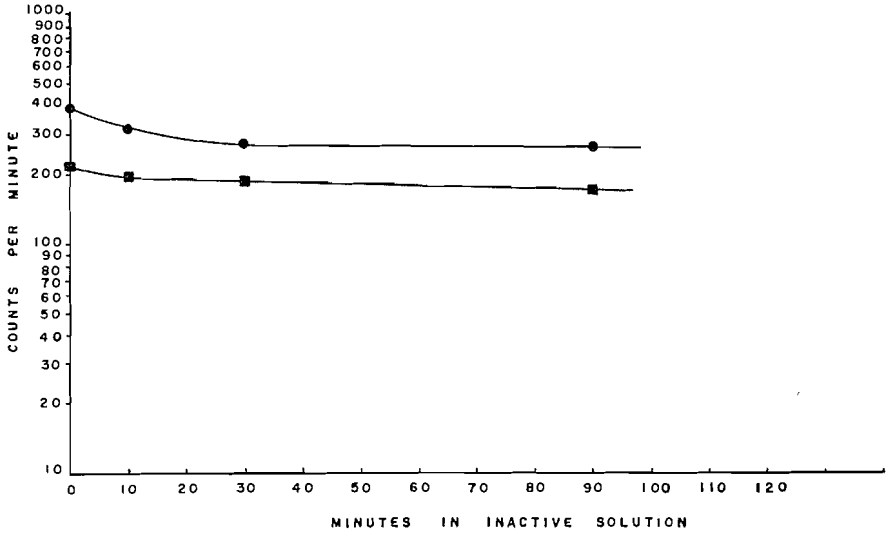

FIG. 14. The deactivation of surfaces with time.
Data from Fig. 7
● —Polished 60 seconds
■ —Polished 600 seconds

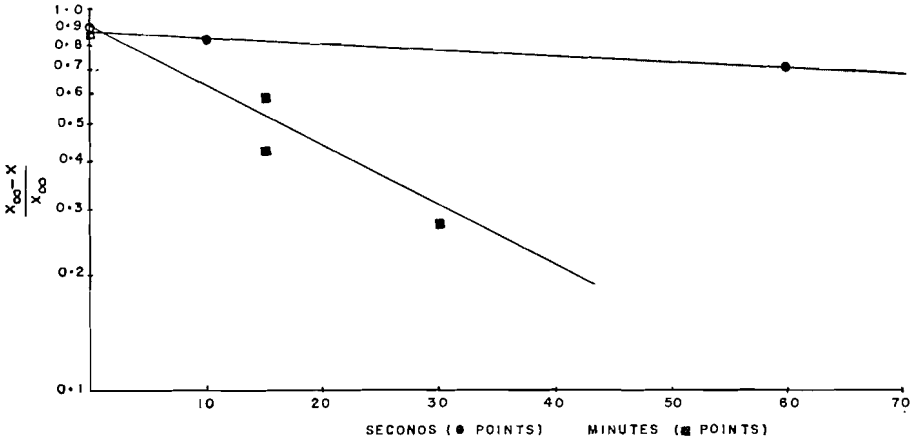

FIG. 15. The uptake of activity in short periods of exposure.
● Data from Fig. 7
■ Data from Fig. 6

regular manner with the passage of time. This might be due to the electrolytic action or to diffusion into the metal or to both. Pitts has derived a log–log equation to explain the exchange between silver salts and a silver solution, and concluded that a diffusion mechanism exists (21). Figs. 12, 13, 14, and 15 show how the data fit the various equations.

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Gerischer and Vielstich calculated from their results the self-diffusion coefficient in silver metal. In view of the above discussion on the state of the metal, it seems to the present authors that what they measured was probably the self-diffusion coefficient in the distorted, worked metal, or along the grain boundaries, where dislocated atoms are also in a much more mobile state than in the interior of the grains (11). They would probably find a difference when they continued their work with single crystals. Winegard and Chalmers measured the self-diffusion of silver along a surface and obtained a value of 2×10^{-9} cm.^{2}/sec. (at 400° C.) (27). They took care in the preparation of their surface (of a single crystal) to avoid forming any "flowed" metal, however.

To recapitulate, the authors, from a study of their own work and that of others who have investigated the exchanges of metals with their ions in aqueous solutions, conclude that such exchanges depend upon the state of the surface. With completely crystalline surfaces, the exchange, if it takes place at all, is of very small extent. Activity is taken up by adsorption, and perhaps by electrodeposition due to small differences of potential between different positions on the crystals. With completely polished surfaces, either the ions from the solution are plated out in a crystalline form while the anodic polish material dissolves, or else a true kinetic exchange takes place, and ions which enter the metal surface from the solution diffuse into the polish layer at a rate very much higher than that of ions in the crystals. With mixed surfaces, partly crystalline and partly amorphous, these processes both occur and in addition there is much electrolytic action between the anodic amorphous material and the cathodic crystalline material.

ACKNOWLEDGMENTS

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THE POLYMERIZATION OF ETHYLENE SENSITIZED BY ETHYL IODIDE[1]

By V. B. Sefton[2] and D. J. Le Roy

ABSTRACT

The polymerization of ethylene sensitized by the thermal decomposition of ethyl iodide in the presence of mercury vapor has been studied at 250°, 275°, and 300°C. C^{14}-labelled ethyl iodide was used in a number of experiments. The increase in the rate of decomposition of ethyl iodide in the presence of ethylene and the formation of butyl iodide are accounted for by equilibrium processes of the type $RI+Hg = R+HgI$. The important features of the reaction were established from the identity, quantity, and activity of the various products. The predominant formation of olefins is attributed to the isomerization and decomposition of large radicals. Very little of the butane is formed by the combination of ethyl radicals. Radical disproportionation is the most important chain termination step.

The decomposition of the lower alkyl iodides has been studied extensively (10) and it is generally agreed that in both the thermal reaction and in the photolysis in the region of the continuum (*ca.* 2600 Å) the primary process consists in the formation of alkyl radicals and iodine atoms. The quantum yields of the photochemical process are low because of the back reaction but can be greatly increased by trapping the iodine atoms with mercury or silver. The thermal or photochemical decomposition of alkyl iodides in the presence of ethylene and either mercury or silver should therefore afford a convenient method for studying the free radical sensitized polymerization of ethylene.

Jungers and Yeddanapalli (5) have studied the polymerization of ethylene sensitized by the photolysis of methyl, ethyl, *n*-propyl, and isopropyl iodides in the presence of mercury at temperatures in the range 130° to 275°C. Under conditions likely to yield low radical concentrations, viz. low iodide concentrations, high ethylene concentrations, and low light intensities, they found that the "yield", defined as the ultimate pressure decrease on prolonged irradiation divided by the initial pressure of iodide, reached maximum values which were in the approximate ratio 3.5 : 3.0 : 2.5 for methyl, ethyl, and the propyl iodides, respectively. They concluded from this that the final polymer had approximately the same molecular weight in each case and that for steric reasons the growing radicals formed by the successive addition of ethylene molecules underwent chain termination when they reached a more or less common critical size. According to their mechanism all the products should be saturated, for at low radical concentrations they assumed that chain termination would take place by the reactions

$$R+C_2H_5I = RH+C_2H_4I \qquad [1]$$

$$C_2H_4I = C_2H_4+I, \qquad [2]$$

while at high radical concentrations they assumed that it would occur by

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radical combination. Radical disproportionation would also be expected to occur, in the light of more recent work (9).

Although Jungers and Yeddanapalli did not analyze their products their conclusions appeared to be well founded. However, because of the fundamental importance of polymerization reactions it seemed desirable to make a further study of the problem taking advantage of fractionation methods and infrared spectra as analytical tools. In the present work the polymerization of ethylene was initiated by the thermal decomposition of ethyl iodide in the presence of mercury. In order to obtain as much information as possible about the reactions of the ethyl radicals a number of experiments were performed using ethyl iodide labelled in the methylene group with C^{14}.

EXPERIMENTAL

The Reaction System

The reaction vessel used in most of the experiments consisted of a Pyrex cylinder having a volume of approximately two liters. The cylinder was mounted vertically and a cooling thimble was placed in the connecting tubing at the point where it emerged from the furnace. By passing compressed air through the thimble the mercury which distilled from the pool at the bottom of the cell was condensed and allowed to drop back into the cell. A mercury cutoff served to isolate the cell during an experiment and this was used as a manometer to give a rough measure of the amount of reaction taking place.

The initial ethyl iodide was measured accurately as a gas, using a separate calibrated volume and a modified Pearson gauge. It was then frozen into the cell by placing liquid air in the thimble. Ethylene was measured and admitted in the same way. The cell was filled at room temperature, and since the reaction was allowed to proceed from $4\frac{1}{2}$ to 38 hr. rapid heating was not considered essential. At the end of an experiment the temperature was lowered by cutting off the current and blowing air through the furnace. When the cell had cooled to approximately room temperature the final pressure was measured and corrected to 25°C.

For the experiments with ethylene and ethyl iodide in the absence of mercury and those with ethyl iodide and mercury in the absence of ethylene a special cell having a volume of 720 $cm.^3$ was used. The reagents were measured as described above and condensed into the cell by immersing it in liquid air. It was then sealed off and placed in the furnace. At the end of an experiment it was sealed to the apparatus at a breakoff valve.

Reagents

The ethylene used had a rated purity of 99.5%. It was treated with 2 *N* ammoniacal silver nitrate to remove traces of acetylene, dried over Drierite and phosphorus pentoxide, and subjected to a number of trap-to-trap distillations.

The inert ethyl iodide was distilled in an 18 plate column and thoroughly degassed before being placed in a storage vessel isolated with a mercury cutoff. The active ethyl iodide, labelled with C^{14} in the methylene group, was

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obtained from Tracerlab. The original 0.3 gm. sample had an activity of one millicurie. It was immediately diluted to 2 gm. with inert ethyl iodide and the portion of this used in the experiments was condensed into a storage bulb and isolated with a mercury cutoff. Both the active and inactive iodides were kept frozen with dry ice to avoid decomposition.

In preparing a sample of active ethyl iodide for an experiment suitable amounts of the active and inactive materials were removed from the storage bulbs, measured in the gas burette, and mixed. An aliquot of this material was then used to obtain the activity of the material to be used in the experiment. In a number of cases aliquots were distilled to remove any active material other than ethyl iodide which might have been present in the original sample. Since no such products could be found the distillation was subsequently eliminated.

Distillation of the Products

Ethylene and ethane were removed by distillation at $-168°$ to $-170°$C. (7). Since no acetylene could be found the second fraction was taken off at an initial pressure of 1.0 mm. (*ca.* $-100°$C.), the cut being made at 0.2 mm. (*ca.* $-50°$C.). The second fraction and the residue remaining in the still were separately treated to remove iodides as described below and then redistilled into a number of fractions using initial and final takeoff pressures of the order of 0.2 and 0.05 mm., respectively. Only for the smaller fractions did the final takeoff temperature exceed the initial by as much as four or five degrees.

Separation and Analysis of the Iodides

A study of the infrared spectrum of the products showed that both ethyl and *n*-butyl iodide were present, although the initial material was free from the latter. Because of their different vapor pressures a fairly complete separation of the two was achieved in the fractionation referred to above. The iodides were removed from the fractions containing them in two ways. In the first method the fractions were frozen onto an aqueous paste of silver metanitrobenzoate which was then allowed to warm to room temperature and stand overnight, resulting in the formation of the ethyl or butyl ester and silver iodide. The residual wet gas was frozen onto solid potassium hydroxide and finally dried for 12 hr. in contact with phosphorus pentoxide. The infrared spectrum of the dried gas showed that the iodides were completely removed by this method.

To determine the amount of ethyl or butyl iodide the mixture of the ester and silver iodide was treated with warm concentrated nitric acid and then diluted with water and centrifuged. The supernatant liquid was then removed. The residual silver iodide was further extracted with 50% aqueous ethanol, filtered, dried, and weighed. Tests on known mixtures of hexane and ethyl iodide showed the method to be accurate to about 2%.

In some of the experiments with active ethyl iodide the silver metanitrobenzoate method was used in an attempt to obtain the activities of the two iodides. In this case the esters were extracted from the silver iodide with petroleum ether. After evaporating the solvent the esters were hydrolyzed

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with 2 *N* sodium hydroxide; the resulting alcohols were then converted to barium carbonate as described below. However, it was found that the silver metanitrobenzoate reagent also removes quantitatively compounds with terminal unsaturation, although it does not remove other olefins to any degree. Although it was apparent that the method could not be used for the determination of the activities of the iodides it was used to remove terminally unsaturated olefins, and this made it possible to determine the activities of the remaining 2-alkenes.

The method ultimately used to determine the activities of the iodides involved their reaction with hexamethylenetetramine in chloroform solution. The resulting quaternary salt is insoluble in chloroform and was filtered off and burned for the activity determinations.

Infrared Gas Analysis

A Perkin-Elmer model 12-C instrument was used, but because of the small samples obtainable the optical arrangement was modified. The glow bar was removed from its normal position to a point on the same optical axis but about 80 cm. from the light chopper. Between the two was placed the cell, consisting of a Pyrex tube 70 cm. long and 15 mm. in diameter. The end near the glow bar was flanged out to about 40 mm. Sodium chloride windows were sealed to each end of the cell and a stopcock and cold finger were sealed to the flanged end for freezing the gas into the cell and for obtaining the blank trace. Despite the very poor optical properties of this arrangement there was an appreciable net improvement in the accuracy with which small samples of gas could be analyzed.

In setting up the quantitative analysis scheme for the hydrocarbons the spectra of a number of standard samples obtained from the United States Bureau of Standards were taken at various pressures. Because of their small extinction coefficients at usable analytical wave lengths the amount of paraffin in a sample was usually determined by subtracting the amount of olefin from the total pressure. These results were checked by taking the spectrum of the residue from the treatment of the olefin–paraffin mixture with mercuric acetate, described below.

Activity Determinations

Samples for combustion were condensed into a gas burette consisting of a number of connected bulbs, one of which contained a cold finger which could be filled with liquid air. After measuring the volume of the gas oxygen was allowed to mix with it by opening a stopcock at the top of the burette. By slowly raising the mercury in the burette the mixture was fed into a continuous stream of pure oxygen which flowed through a conventional microcombustion tube. The carbon dioxide formed was bubbled through saturated barium hydroxide solution. The barium carbonate was collected and washed on a filter paper held in a Tracerlab E-8A precipitation apparatus. Carbon numbers calculated from the weights of dried barium carbonate were usually a few per cent low, presumably because of incomplete trapping of the carbon dioxide in the barium hydroxide solution.

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The C^{14} activity of the ethyl iodide used in any particular experiment was arbitrarily given a value $A = 1$, and the activities of the various products were measured relative to this on a molar basis. To obtain A the measured number of counts per minute, C_{obs}, was first corrected for the background count C_b. A correction for self-absorption was then made using the data of Yankwick *et al.* (12). For a constant area of barium carbonate precipitate (2.83 cm.^{2}, compared to our value of 2.82 cm.^{2}) having various weights per unit area X, they obtained a function $J(X)$ such that $(C_{obs}-C_b)/J(X)$ is equal to the number of counts per minute corrected for background and self-absorption. To allow for any variation in the sensitivity of the geiger tube the count on the sample was always followed by one, C^*, taken on a standard reference sample of barium carbonate using the same geometry. A quantity S, proportional to the specific activity of the sample, was then obtained,

$$S = \frac{(C_{obs}-C_b)/J(X)}{(C^*-C_b)W},$$

in which W is the weight of barium carbonate in the sample. The molar activity of the sample relative to that of the ethyl iodide used, referred to in the text simply as molar activity, is then given by

$$A = (S_s/S_i)\ N/2,$$

in which the subscripts s and i refer to the sample and to the iodide, respectively, and N is the number of carbon atoms in a molecule of product. A typical result, found for the hexane obtained in one of the experiments, is illustrated in Table I. The value of the molar activity of the hexane indicates that it contains, on the average, one ethyl radical derived from ethyl iodide.

TABLE I

DETERMINATION OF THE MOLAR ACTIVITY OF HEXANE

Material	W, mgm.	X, mgm./cm.^{2}	$J(X)$	$C_{obs}-C_b$, c.p.m.	C^*-C_b, c.p.m.	S	A
Initial ethyl iodide	20.6	7.32	0.421	12570	4370	0.331	1.00
Hexane	31.48	11.18	0.300	4350	4410	0.1045	0.95

Separation of Olefins from Paraffins

To determine the molar activity of a paraffin it was necessary to separate it from the unsaturated compounds present in the same fraction. This was accomplished by an adaptation of the hydroxy-mercurial method (8). The gas was frozen into a 100 ml. flask containing 20 ml. of saturated aqueous mercuric acetate and 10 ml. of 3% hydrogen peroxide which had previously been degassed. The flask was then warmed to room temperature and shaken, intermittently, over a period of 12 hr. The residual gas and 1 or 2 ml. of the liquid were then distilled onto solid potassium hydroxide. After several hours the contents were cooled with dry ice and the hydrocarbons distilled back into the system and measured. For compounds of higher molecular weight than bu-

tane the final drying was made with phosphorus pentoxide rather than dry ice. The infrared spectra showed complete removal of olefins by this method. Analysis of synthetic mixtures showed the method to be quantitative for mixtures of ethane and ethylene. For other olefin–paraffin mixtures there was a slight loss of paraffin; in these cases the quantity of paraffin was estimated by the infrared method.

Nonvolatile Products

After a series of experiments in which ethylene, ethyl iodide, and mercury had been used the nonvolatile material in the reaction vessel was extracted with carbon tetrachloride. The absence of an appreciable residue on evaporating the solvent indicated that no diiodoethane was present. Except for the mercury, the nonvolatile material was completely soluble in aqueous potassium iodide. Chemical tests showed the presence of mercurous iodide. The absence of diiodoethane was also confirmed in the experiments with ethyl iodide and mercury alone.

RESULTS

Products

In Table II are shown the results of pairs of experiments done at 250°, 275°, and 300°C. The amounts of the products are given in mm. pressure in the reaction vessel at 25°C. The values of $-\Delta P/-\Delta C_2H_5I$, analogous to the

TABLE II

PRODUCTS OF THE REACTION

	250°C.		275°C.		300°C.	
Experiment No.	23	27	21	22	28	25
Initial C_2H_5I	10.4	33.2	11.2	34.9	11.3	32.0
Initial C_2H_4	139.6	154.3	143.5	143.6	146.2	152.5
Time, hr.	25	24	19	17.5	7	8
$-\Delta C_2H_5I$	8.8	29.3	10.6	34.1	10.8	30.8
$-\Delta C_2H_4$	30.9	61.4	41.3	76.0	46.4	78.0
Ethane	0.64	2.04	0.5	3.6	0.9	3.6
Propane	—	0.2	—	0.37	0.38	1.5
n-Butane	0.89	2.9	2.2	6.3	2.3	7.0
Hexane	1.5	3.7	2.8	4.5	2.4	4.9
Total paraffin obs.	3.0	8.8	5.5	14.8	6.0	17.0
Total paraffin calc.	3.6	12.2	5.0	16.6	5.4	15.4
Propylene	0.54	0.67	1.73	2.0	3.7	5.2
Butene-1	1.87	2.1	2.5	3.2	3.1	5.2
trans-Butene-2	0.48	0.35	0.62	0.9	1.3	1.7
2-Methyl butene-1	1.22	0.67	1.8	1.1	1.9	1.7
Hexene-1	0.42	2.1	0.54	1.4	1.0	1.9
trans-Hexene-2	0.47	1.5	0.90	2.1	1.7	3.3
C_7 and higher	5.5	11.5	4.9	13.0	4.5	7.2
Total olefin obs.	10.5	18.9	13.0	23.7	17.2	26.2
Total olefin calc.	9.9	15.5	13.5	21.9	17.8	27.8
Butyl iodide	1.7	5.0	0.6	1.0	0.0	0.0
$-\Delta P$	25.5	59.5	32.9	69.3	33.5	65.6
$-\Delta P/-\Delta C_2H_5I$	2.9	2.4	3.1	2.0	3.1	2.1
Olefin/paraffin obs.	3.5	2.1	2.4	1.6	2.9	1.5
Olefin/paraffin calc.	2.7	1.3	2.7	1.3	3.3	1.8

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"yield" of Jungers and Yeddanapalli (5), are seen to be sensitive to the initial iodide pressure but relatively insensitive to temperature, in agreement with their observations. The value of approximately three for low iodide pressures is identical with their value for low ethyl radical concentrations. However, instead of the products being all saturated, as they predicted, it is seen that there is considerably more olefin than paraffin. The proportion of olefin is greater for low than for high ethyl iodide concentrations, and even in the latter case the amount is greater than could be accounted for by disproportionation.

Qualitative infrared analysis of the fraction listed in Table II as "C_7 and higher" showed it to be composed of hydrocarbons containing the groups $CH_2{=}\underset{\displaystyle R'}{\overset{\displaystyle |}{C}}{-}R$ and $CH_2{=}CHR$, in which R and R′ are saturated radicals. The amount of this fraction was determined as the difference between the total final pressure and the sum of remaining individual product pressures. From the carbon balance of the reagents and products the average carbon number of this fraction was found to be approximately nine.

After treating the C_6 fraction with mercuric acetate it was possible to identify a hydrocarbon having an important band at 10.10 microns. Because of the small amount present it could not be positively identified, although the spectrum strongly resembled that of methyl cyclopentane. It was estimated that it could have amounted to 10 to 20% of the C_6 "paraffin".

Since the only products formed were alkanes, mono-olefins, cycloparaffins, and butyl iodide, it follows that the amount of paraffin produced must be equal to one half of the difference between the amount of ethyl iodide consumed and the amount of butyl iodide formed. The values of "Total paraffin calc." listed in Table II were obtained in this way; "Total olefin calc." was obtained by difference.

No evidence could be found for either methane or hydrogen. Pentane, if formed, did not exceed 5% of the sum of butane and hexane. The maximum amounts of pentene-1, cyclopentane, or cyclohexane that could be present were estimated to be less than 0.1 mm. The amount of *cis*-butene-2 could not exceed 20% of the *trans* isomer. The maximum amount of hydrogen iodide was estimated to be less than 0.01 mm.

Isotope Effect in the Decomposition of Ethyl Iodide

An appreciable carbon isotope effect has been observed in the thermal decomposition of a number of organic compounds (4) in which the decomposition has involved the rupture of C—C bonds. In the present instance a rupture of a C—I bond is involved. In most of the experiments a large part of the ethyl iodide was decomposed and hence, even if there were an isotope effect, the proportion of C^{14} in the ethyl radicals formed would be approximately the same as in the original ethyl iodide. However, the proportion of inactive ethyl radicals might be greater at the beginning of an experiment when the ethyl radical concentration is higher and the instantaneous value of the

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"yield" is lower. Erroneous conclusions might therefore be drawn from the final measured activities of the products. To ascertain if the isotope effect were significant experiments were performed in which considerably different amounts of active ethyl iodide were decomposed in the presence of mercury but in the absence of ethylene. The results are shown in Table III. The activities are given in terms of the quantity S, defined previously. It is clear from the table that the variations in S are within the probable error of its determination and that the decomposition of ethyl iodide does not involve an appreciable isotope effect.

TABLE III

DECOMPOSITION OF C^{14}-LABELLED ETHYL IODIDE IN THE PRESENCE OF MERCURY

Experiment No.	31	32
Temperature, °C.	250	300
Initial ethyl iodide, mm.	38.6	39.2
Final ethyl iodide, mm.	36.2	24.0
Time, hr.	11	4.5
Ethylene formed, mm.	0.8	1.8
Ethane formed, mm.	1.2	7.1
Butene formed, mm.	—	0.4
Butane formed, mm.	—	1.6
S for initial iodide:		
1st sample	0.398	0.418
2nd sample	0.385	0.389
S for final iodide	0.384	0.404
S for C_2 fraction	0.378	0.410
S for C_4 fraction	—	0.395

TABLE IV

MOLAR ACTIVITIES OF THE PRODUCTS

	250°C.							275°C.	
Experiment No.	11	13	14	12	17	27	15	21	29
Initial ethyl iodide, mm.	30.4	77.9	4.0	10.7	24.5	33.2	34.0	11.2	34.2
Initial ethylene, mm.	69.4	69.5	141.2	137.8	136.8	154.3	134.5	143.5	151.3
Time, hr.	15	16	16.5	16	38	24	17	19	6.8
Ethane formed, mm.	1.2	4.7	—	0.4	1.9	2.0	1.8	0.5	2.5
Ethylene formed, mm.*	0.4	1.0	—	1.1	0.8	0.5	0.4	0.9	—
Total alkanes formed, mm.	5	8	—	—	9	12	10	5	15
Butyl iodide formed, mm.	21.4	61.5	2.3	5.3	—	5.0	—	0.6	—
Ethane	1.0	1.0	—	0.89	0.83	1.0	0.89	0.83	1.05
Propylene	—	—	—	—	0.30	—	—	0.36	0.36
Butane	0.92	1.1	0.56	0.8	0.94	0.92	0.88	0.74	1.04
Butene-1 / *trans* Butene-2†	0.4	—	—	—	0.1	0.4	0.3	0.5	0.4
2-Methyl butene-1	—	—	—	—	—	0.4	—	0.5	—
Hexane	0.99	0.94	0.72	0.72	0.87	0.96	0.96	0.69	—
Hexene-1 / *trans* Hexene-2†	—	—	—	—	0.87	0.9	0.84	0.69	—
C_7 and higher‡	1.7	1.7	—	1.04	1.2	—	1.08	1.1	—
Butyl iodide	—	—	—	—	—	0.7	—	—	0.6

**Amount present with molar activity of unity.*
†Calculated from composition of fraction and activities before and after removing olefin.
‡Based on an average carbon number of nine.

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Activity of the Products

The results of a series of experiments using active ethyl iodide are shown in Table IV.

The use of a tracer does not make it possible to determine the amount of ethylene *formed* in the reaction since it might not have originated from ethyl iodide. However, the minimum amount formed can be estimated on the assumption that it would have a molar activity of unity. The values given in Table IV for ethylene formed were obtained in this way. About all that can be said with certainty is that some ethylene is formed and that its amount is probably of the same order as that of the ethane.

Experiments 11 and 13 are of particular interest because of the very large amounts of *n*-butyl iodide formed when the concentration of ethyl iodide approaches that of the ethylene.

DISCUSSION

One would infer from previous work that the initial process involves the decomposition of ethyl iodide into an ethyl radical and an iodine atom. However, a comparison of the results of experiment 31 (Table III) and experiment 27 (Table II) shows that the presence of ethylene greatly accelerates the rate of decomposition of ethyl iodide, which suggests that equilibria of the following type may be involved.

$$C_2H_5I + Hg \rightleftharpoons C_2H_5 + HgI \quad [3]$$

$$C_2H_5I + HgI \rightleftharpoons C_2H_5 + HgI_2 \quad [4]$$

The addition of ethylene would lower the ethyl radical concentration and accelerate the decomposition of ethyl iodide.

Although the initial stages of the polymerization of ethylene undoubtedly consist in the successive addition of ethylene to ethyl radicals, a number of possible steps can be suggested for the formation of the ultimate products from the linear 1-alkyl radicals produced in this way.

(*i*) *Reaction with Ethyl Iodide to Form a Linear Alkane* (*Reaction* [1])

It has been suggested by a number of workers that reactions of this type play an important role in the photolysis of ethyl iodide (5, 11). However, their evidence is by no means convincing. West and Schlessinger (11) found that methylene iodide was formed in the photolysis of methyl iodide provided no "getter" was used to trap the iodine; in the presence of silver none was formed. In the case of ethyl iodide they found no ethylene iodide under either circumstance. Jungers and Yeddenapalli (5) did not subject their products to chemical analysis, but simply quoted the results of West *et al.* as showing that [1] would occur at high concentrations of ethyl iodide. We were unable to find ethylene iodide under any conditions.

If it were formed, the radical C_2H_4I could conceivably disappear in a number of ways. If it decomposed to form ethylene and an iodine atom, or if it reacted with mercury to form ethylene and mercurous iodide, then 1 mole of active

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ethylene would have to be formed for every mole of alkane formed by [1] or every mole of ethyl iodide decomposed by [1]. However, it is evident from Table IV that the amount of ethylene formed with a molar activity of unity did not exceed one-eighth of the total alkanes even at high concentrations of ethyl iodide. The possibility that the C_2H_4I radical could react with ethyl iodide to form ethylene iodide can be eliminated since the latter was not formed. If it reacted with alkyl radicals to form higher alkyl iodides, then these, in particular butyl iodide, would be expected to have a molar activity of two, which was not the case. Furthermore, in experiments 11 and 13 (Table IV) the amount of butyl iodide formed far exceeded the amount of alkanes produced, which could not be the case if reaction [1] had occurred. A suggested mechanism for the formation of butyl iodide will be given later.

(*ii*) *Combination of Radicals to Form Linear Alkanes*

It is evident from the olefin/paraffin ratios given in Table II that this process does not play a leading role. It can also be shown that only a small proportion of the paraffin could be formed in this way. The molar activity of the butane is much less than two. If it were formed by the combination of ethyl radicals a considerable proportion of the latter would have to be inert, i.e. arise from processes other than the decomposition of ethyl iodide. Since it is reasonable to assume that ethane is formed from ethyl radicals, it would follow that the molar activity of the ethane would have to be of the order of 0.5 or less, in disagreement with the data of Table IV. The same argument applies to the formation of hexane and higher paraffins.

(*iii*) *Disproportionation of Radicals to Form Alkanes and Either Cycloparaffins or Olefins*

This process would lead to olefin/paraffin ratios of unity or, if any combination took place as well, less than unity. While disproportionation cannot account for the major part of the olefin (and cycloparaffin) it can account for the alkanes and the corresponding amount of olefin.

(*iv*) *Hydrogen Abstraction from Olefins*

Reactions of this type can be discounted since the radicals of the vinyl type formed in this way would be certain to yield, ultimately, some diolefin, and no evidence for this could be obtained.

(*v*) *Decomposition of Radicals to Yield Olefins or Cycloparaffins, and an Alkyl Radical*

Reactions of this type must account not only for the compounds having an odd number of carbon atoms but also for the major portion of the olefin produced. It is readily seen, however, that a simple C—C bond rupture followed by the isomerization of the biradical is not the most probable process, as only inert olefins would be formed in this way.

If the observed olefin activities were due to disproportionation reactions, which involve two radicals, then the ratio of active to inactive butene would be expected to increase markedly with the radical, i.e. the ethyl iodide, concentration. Evidence for this is not conclusive. The results of experiments 17, 27, and 15 given in Table IV indicate an increase in the activity of the butene when

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the ethyl iodide pressure is increased, but similar experiments at 275°C. show a decrease in the molar activity of the butene from 0.5 to 0.4 when the ethyl iodide pressure is increased from 11.2 to 34.2 mm.

In their experiments on tetramethylene biradicals Bawn and Milsted reported "butylene" as one of their products but did not identify the particular isomer (2). Benson and Kistiakowsky (3), on the other hand, found cyclobutane to be the only C_4 product from the photolysis of cyclopentanone and questioned the previous conclusions of Norrish *et al.* (1). It seems likely, therefore, that if tetramethylene biradicals were formed by the decomposition of a linear alkyl radical some evidence of cyclobutane would be found. This was not the case.

Kossiakoff and Rice (6) have pointed out that in many cases the activation energy for the isomerization of a long-chain free radical is much less than the activation energy for its decomposition and that as a result there should be an equilibrium process involving isomeric forms of the free radical. In particular, they suggest that 1-hexyl radicals should isomerize readily by a 1–5 shift of the free valence to form 2-hexyl radicals. Furthermore, the latter should decompose more readily than the 1-hexyl isomer since propylene and a propyl radical would be formed in a single step. The propylene formed in this way would be active.

It is evident that 1-hexyl-5-C^{14} radicals can give rise to 2-hexyl-2-C^{14} radicals by a 1–5 shift of the free valence, or to 1-hexyl-2-C^{14} radicals by a 1–6 shift. The latter could isomerize to 2-hexyl-5-C^{14} by a 1–5 shift. Similar considerations may be applied to other large radicals. Their disproportionation will yield paraffins and olefins with molar activities of unity; their decomposition will yield olefins with molar activities less than unity.

Isomerization of 1-alkyl radicals is undoubtedly involved in the formation of olefins containing the group $CH_2{=}\underset{\displaystyle R'}{\overset{\displaystyle |}{C}}{-}R$. If the 2-methyl butene-1 were produced by the addition of (active) ethyl radicals to propylene, followed by the disproportionation of the resulting 2-methyl butyl-1 radical with another radical, then its molar activity would be at least as great as unity. The observed activity of less than 0.5 suggests that it arises through the addition of ethylene to 2-hexyl-2-C^{14} or 2-hexyl-5-C^{14} radicals, followed by a 1–7 and then a 1–5 shift of the free valence. Subsequent decomposition of the radical could yield either 2-methyl butene-1 and a propyl radical, or 2-methyl hexene-1 and a methyl radical. The molar activity of the pentene would be less than that of the heptene. As mentioned previously, evidence for compounds of the latter type was found in the "C_7 and higher" fraction.

The postulate that radical decomposition is usually preceded by isomerization of the original 1-alkyl radicals also affords an explanation for the fact that the activities of the ethane and butane are slightly less than unity. The decomposition of large radicals into olefins will give rise to some radicals having molar activities less than unity. The ethane and butane formed by the disproportionation of ethyl or butyl radicals with larger radicals will then have activities somewhat less than unity. This is supported by the fact that in any

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particular experiment the molar activities of the ethane and butane were closely related, as shown in Table V. It is also seen that the activities of these

TABLE V

COMPARISON OF MOLAR ACTIVITIES OF ETHANE AND BUTANE

Expt. No.	Temp., °C.	Molar activity of ethane	Molar activity of butane	Olefin/paraffin calc.
27	250	1.0	0.92	1.3
21	275	0.83	0.74	2.7
28	300	0.71	0.68	3.3

products are lower in the experiments in which the olefin/paraffin ratio was high, i.e. in the experiments in which radical decomposition was more important.

(*vi*) *Formation of Butyl Iodide*

It is significant that no butyl iodide was formed in the absence of ethylene. Also, its molar activity is less than unity, whereas it would be greater than unity if it were formed by the reaction

$$C_2H_5+C_2H_4I = C_4H_9I. \quad [5]$$

In experiments performed at 250°, 275°, and 300°C. with ethyl iodide and ethylene but in the absence of mercury there was no butyl iodide formed, which shows that its method of production is not through the reaction

$$C_2H_5I+C_2H_4 = C_4H_9I. \quad [6]$$

Evidence has already been given to show that the decomposition of ethyl iodide in the presence of mercury and the mercury iodides involves equilibrium processes. If so, butyl radicals could take part in similar equilibria, viz.,

$$C_4H_9+HgI = C_4H_9I+Hg \quad [7]$$

$$C_4H_9+HgI_2 = C_4H_9I+HgI. \quad [8]$$

Reactions of this type appear to afford the most satisfactory explanation for the formation of butyl iodide. The fact that its molar activity is somewhat less than that of the butane suggests that a small amount of the latter is probably formed by the combination of ethyl radicals.

SUMMARY

The use of C^{14}-labelled ethyl iodide together with extensive chemical analysis of the products has revealed a number of features of the ethyl iodide sensitized polymerization of ethylene not previously established. Some of these features apply specifically to the use of alkyl iodides as sources of free radicals while others would be expected to apply quite generally to the free radical sensitized polymerization of olefins.

The primary process in the presence of mercury has long been considered to be a C—I bond rupture, followed by the reaction of the iodine atom with mercury,

$$RI = R+I \quad [9]$$

$$I+Hg = HgI. \quad [10]$$

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However, the fact that butyl iodide was only formed in the presence of mercury (and ethylene), and the fact that ethylene accelerates the rate of decomposition of ethyl iodide suggest that [11] is the primary process in the decomposition of alkyl iodides.

$$RI + Hg \rightleftharpoons R + HgI \qquad [11]$$

It is evident that if [10], as well as [9], is considered to be a reversible process then in the absence of reactions other than those indicated it is immaterial whether [9] or [11] is considered to be the primary process, since $K_{11} = K_9 \cdot K_{10}$.

The present experiments confirm previous evidence that larger 1-alkyl radicals are built up by the successive addition of ethylene to ethyl radicals,

$$C_2H_5 + C_2H_4 = C_4H_9 \qquad [12]$$

$$C_4H_9 + C_2H_4 = C_6H_{13}, \qquad [13]$$

etc.

The concentrations of the radicals would be expected to decrease in the order ethyl, butyl, hexyl, etc., since radical growth can be terminated at any stage. This is in keeping with the fact that butyl iodide was formed (by the reverse of [11]), but not hexyl or higher iodides.

The large olefin/paraffin ratios and the formation of products containing an odd number of carbon atoms show that the decomposition of large radicals into olefins and smaller alkyl radicals plays a major role under the experimental conditions used. Furthermore, the structures and molar activities of these olefins indicate that in many cases the large 1-alkyl radicals isomerize by 1–5 and 1–6 (and presumably other) shifts of the free valence before they decompose. As would be expected, the radical decomposition reactions are more important at low than at high radical concentrations.

Chain termination occurs by both combination and disproportionation of radicals, but the latter appeared to be the more important.

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THE EFFECT OF ATMOSPHERE DEPLETION IN SPHERICAL DIFFUSION FLAMES[1]

By R. J. Cvetanović

ABSTRACT

Solutions of the second order non-linear differential equation of spherical diffusion flames have been obtained for the range of conditions of experimental interest. Deviations from the simplified exponential solution are presented in a form suitable for their direct evaluation. Some recent contributions to the theory of the method are discussed.

INTRODUCTION

The diffusion flame method of Hartel and Polanyi (5) is used for determination of the rate constants of some fast gas reactions. It is based on a comparison of the rate of reaction with the rate of diffusion of one of the two reactants. The latter is introduced through a nozzle into the reaction zone where it spreads by diffusion and encounters the other reacting substance, the "atmosphere reactant". The original theoretical treatment of the method implied the following three simplifying assumptions:

1. The mass flow of the two reactants can be neglected.
2. There is a spherical symmetry in the distribution of the nozzle reactant in the reaction zone.
3. The concentration of the atmosphere reactant is constant throughout the reaction zone.

In the steady state the general diffusion equation reduces then to the form

$$[1] \qquad \frac{d^2y}{dr^2} + \frac{2}{r}\frac{dy}{dr} - \frac{k_p}{D_y} yz = 0$$

where y and z are the concentrations of the nozzle and the atmosphere reactant, respectively, D_y is the diffusion coefficient of the former in the gas mixture, k_p is the value of the rate constant to this approximation, and r is the radius of the spherical reaction zone. Since z is assumed constant and equal to z_∞, the concentration outside the reaction zone, and y vanishes as $r \to \infty$, the solution of [1] is

$$[2] \qquad y = (A_p/r)\exp(-rC_p), \qquad \text{where } C_p = (k_p z_\infty/D_y)^{\frac{1}{2}}.$$

From the values of y, y_1, and y_2 at two points, r_1 and r_2 ($r_2 > r_1$), the rate constant can be calculated using the expression

$$[3] \qquad C_p = \ln(y_1 r_1/y_2 r_2)/(r_2 - r_1).$$

Since its introduction in 1930 the diffusion flame method has been widely used and a large number of experimental determinations have been reported

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in the literature. The method was originally devised and is particularly suited for determination of the rates of reaction of sodium atoms, which are introduced into the reaction zone through the nozzle in a stream of an inert carrier gas. The extent of penetration of sodium in the reaction zone for given steady state conditions is established by optical means. An important extension of the method has recently been proposed by Kistiakowsky and his co-workers (2, 3), who based the evaluation of the rate constant on an exploration of the temperature pattern of the spherical reaction zone. The particular significance of the temperature pattern method lies in its potential applicability to a wider variety of processes, possibly also to some atomic and free radical reactions which may be difficult to evaluate quantitatively by other means.

At present, it appears impossible to treat mathematically the general case of a diffusion flame and take into account all the details of the process. The quantitative usefulness of the spherical diffusion method depends, therefore, on how closely the simplified model suggested by Hartel and Polanyi can be approached experimentally. After the early realizations of a large uncertainty in this respect, a thorough empirical study by Heller (6) resulted in a specification of the ranges of experimental conditions within which the simple model was considered valid to a good approximation. An attempt to extend the use of the method to very fast reactions (4) resulted in the observation of the formation of "core" flames, the flames assumed to contain a core of unreacted sodium into which no atmosphere reactant did penetrate. The calculated rate constants were strongly pressure dependent and a drastic change in experimental conditions was necessitated.

In a previous paper (1) a more elaborate model was considered and the theoretical treatment extended to take into account the fact that the atmosphere reactant is consumed in the reaction and its concentration is not constant in the reaction zone. It was shown that when the mass flow of the reactants is neglected, the spherical diffusion process is described by the differential equation

$$[4] \qquad \frac{d^2y}{dr^2} + \frac{2}{r}\frac{dy}{dr} - \frac{k}{D_z}y^2 + \frac{ky_1r_1}{D_z}\frac{y}{r} + \frac{k(z_\infty - z_1)r_1}{D_y}\frac{y}{r} - \frac{kz_\infty}{D_y}y = 0,$$

where D_z is the diffusion coefficient of the atmosphere reactant and z_1 its concentration at some particular value of the radius (r_1), and of which Equation [1] is a special case. Analysis of the derived expressions and of the single numerical solution available at the time for a particular set of experimental results showed that for relatively slower reactions the effect of the depletion of the atmosphere reactant by virtue of its consumption in the reaction was not large and that more appreciable effects could be expected for very fast reactions. Any quantitative conclusions in this respect, however, required solutions of Equation [4] for a wide variety of experimental conditions.

A function representing the generalized solution of Equation [4] has now been tabulated for selected cases covering the range of experimental interest. In the present article summarized results of the performed computations are given and their implications discussed.

Solutions of the Non-linear Differential Equation of the Spherical Diffusion Process

The radius r_1 and the corresponding concentrations of the two reactants, y_1 and z_1, in Equation [4] are in no way specified. It is, therefore, permissible to take for r_1 the particular value of r at which $z_1 = 0$, without having to consider, for the moment, how the values of y_1 and r_1 can be ascertained. Defining r_1 in this manner and writing

$$[5] \quad v = \frac{r}{r_1}\,\frac{yD_y}{y_1D_y+z_\infty D_z},\quad x = \frac{r}{r_1}\,\frac{z_\infty D_z}{y_1D_y+z_\infty D_z},\quad K = \frac{kz_\infty}{D_y}\left(\frac{r_1}{x_1}\right)^2 = C^2\left(\frac{r_1}{x_1}\right)^2$$

and consequently

$$[6] \quad x(r_1) = x_1 = 1/(1+y_1\,D_y/z_\infty\,D_z), \quad 0 < x_1 < 1, \quad v(x_1) = v_1 = 1-x_1,$$

the differential Equation [4] is transformed into the following generalized non-dimensional form

$$[7] \qquad \frac{d^2v}{dx^2} = \frac{Kv}{x}(v+x-1).$$

In view of the relations [6] and subject to the condition that $v \longrightarrow 0$ when $x \longrightarrow \infty$, the solution of [7] is

$$[8] \qquad v = \phi(K, x_1, x).$$

The function v has been tabulated for the following values of K and x_1:

x_1	Values of K										
.99	.001	.005	.01	.05	.1	.5	1	5			
.8	.001	.005	.01	.05	.1	.5	1	5			
.6		.005	.01	.05	.1	.5	1	5	10		
.4			.01	.05	.1	.5	1	5	10		
.2				.05	.1	.5	1	5	10	50	100
.1					.1	.5	1	5	10	50	100

The solutions have been obtained numerically by the Computation Centre of the University of Toronto and the details of the computational technique employed are given elsewhere (9). The tables of the computed values will be supplied on request. They lend themselves to graphical interpolation and can be readily used for the calculation of the rate constants for any of the usual experimental conditions. For most experimental applications, however, the graphs and the tables in the following section will give directly the magnitude of the deviation from the rate constants obtained from the simplified exponential solution given in Equations [2] and [3].

Deviations from the Exponential Solutions

(*a*) *The Diffusion Flame Method (The "Two-point Boundary" Method)*

The rate constants, k_p, obtained from the exponential solution can be calculated from Equation [3]. Taking into account relationships [5] and [6] it is readily seen that

$$[9] \qquad \delta = \frac{k}{k_p} = K(x_2-x_1)^2 \Big/ \left(\ln\frac{v_1}{v_2}\right)^2.$$

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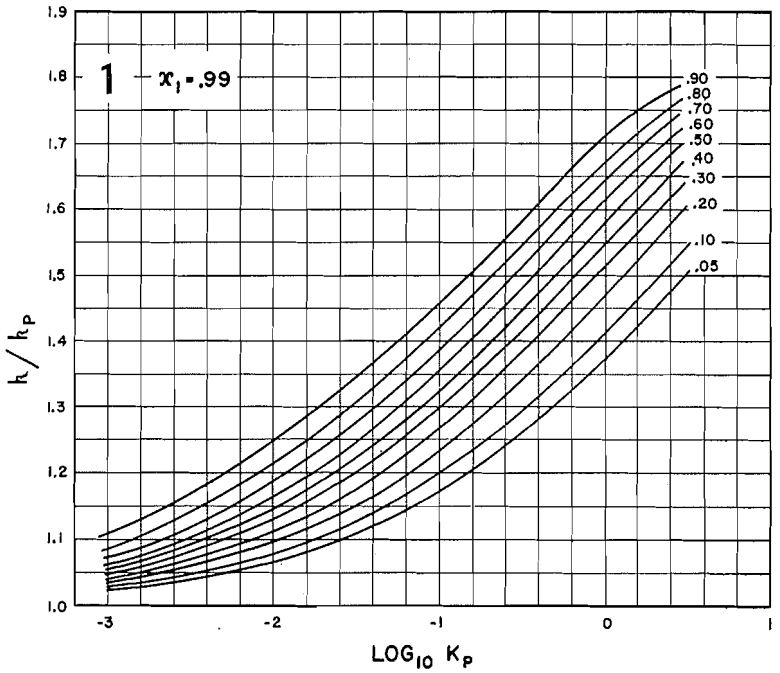
The correction factor δ is a function of K, x_1, and x_2 or, equally well, of K, x_1, and v_2. It was found convenient to calculate and plot the values of δ for



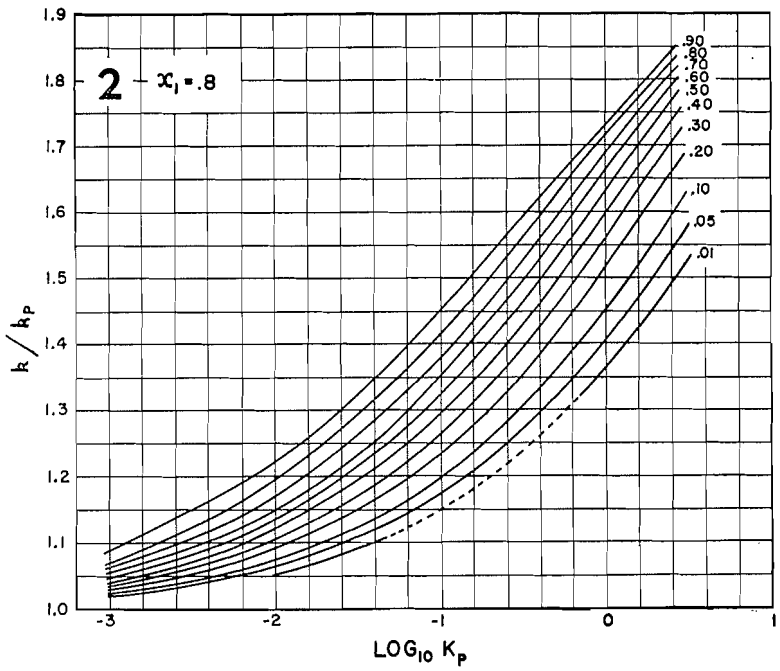


FIG. 1. Deviation factors for $x_1 = 0.99$. The numbers on the curves are v_2/v_1 ratios.
FIG. 2. Deviation factors for $x_1 = 0.8$. The numbers on the curves are v_2/v_1 ratios.

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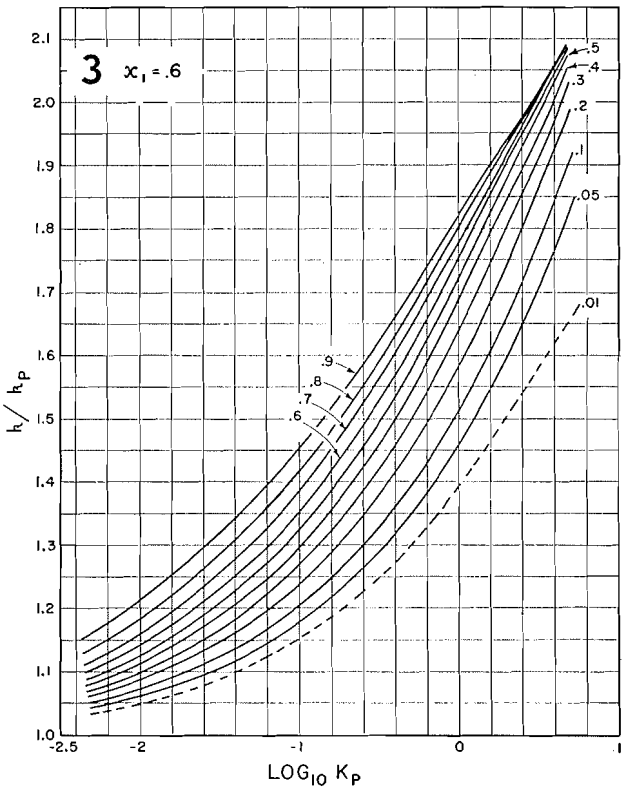
various K and x_1 values at different v_2/v_1 ratios. For $x_1 = 0.99$, 0.8, 0.6, and 0.4 the correction factors are given in Figs. 1–4; the numbers on the curves



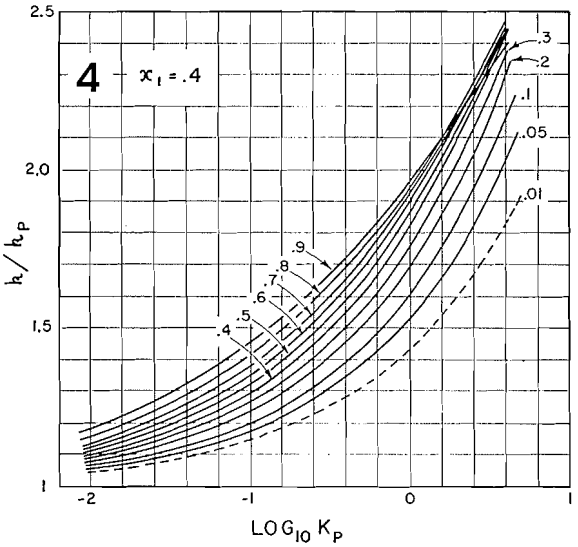


FIG. 3. Deviation factors for $x_1 = 0.6$. The numbers on the curves are v_2/v_1 ratios.
FIG. 4. Deviation factors for $x_1 = 0.4$. The numbers on the curves are v_2/v_1 ratios.

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are the v_2/v_1 ratios. For $x_1 = 0.2$ and 0.1 the correction factors are given (as a function of K and v_2/v_1) in Table I, since small scale plots were not feasible

TABLE I

DEVIATION FACTORS ($\delta = k/k_p$) FOR $x_1 = 0.2$ AND 0.1, FOR DIFFERENT K AND v_2/v_1 RATIOS

v_2/v_1	K							
	0.05	0.1	0.5	1	5	10	50	100
				$x_1 = 0.2$				
.90	1.28	1.38	1.72	1.96	2.76	3.29	5.21	6.33
.80	1.25	1.35	1.69	1.93	2.80	3.41	5.89	7.61
.70	1.23	1.32	1.66	1.89	2.81	3.49	6.57	9.10
.60	1.22	1.30	1.62	1.85	2.79	3.51	7.13	10.55
.50	1.20	1.28	1.59	1.81	2.75	3.49	7.48	11.62
.40	1.19	1.26	1.55	1.77	2.68	3.42	7.56	12.05
.30	1.17	1.24	1.51	1.72	2.58	3.30	7.35	11.78
.20	1.15	1.22	1.47	1.65	2.46	3.12	6.85	10.84
.10	1.13	1.19	1.41	1.57	2.27	2.85	5.97	9.19
.05	1.12	1.17	1.36	1.51	2.12	2.63	5.27	7.88
				$x_1 = 0.1$				
.90		1.35	1.79	2.11	3.50	4.65	9.98	14.54
.80		1.32	1.74	2.06	3.53	4.86	12.78	20.82
.70		1.30	1.70	2.02	3.51	4.92	14.42	25.73
.60		1.28	1.66	1.97	3.44	4.86	14.98	27.62
.50		1.27	1.63	1.91	3.33	4.71	14.62	27.07
.40		1.25	1.59	1.86	3.19	4.49	13.66	24.99
.30		1.23	1.54	1.79	3.02	4.20	12.30	22.01
.20		1.21	1.49	1.72	2.81	3.85	10.61	18.42
.10		1.18	1.43	1.62	2.54	3.37	8.53	14.18
.05		1.16	1.38	1.55	2.34	3.03	6.81	—

because of overlapping of some of the curves. In Figs. 1 to 4 δ is plotted against K_p, where

$$K_p = K/\delta = C_p^2(r_1/x_1)^2, \quad [10]$$

and not against K, because K_p can be readily calculated for given experimental conditions as well as x_1 and v_2/v_1, and the use of the graphs is thus made quite simple. The values of the rate constants are obtained from the relationship $k = k_p \times \delta$, after calculating k_p from Equation [3] and establishing δ by the use of the graphs.

(*b*) *The Concentration Pattern Method*

In the application of the "temperature pattern" method of Garvin and Kistiakowsky (3) a quantity proportional to the product of the concentration of the nozzle reactant and r at different values of r is obtained experimentally. Inasmuch as the exponential solution [2] is valid, a plot of $\log_e$ of this quantity against r should yield a straight line the slope of which is equal to $(-C_p)$. Equally well, a plot of $\log_e v$ against x would result in a straight line with a slope of $(-C_p r_1/x_1)$. The latter plots for some of the computed cases are given in Figs. 5–8, in which $\log_{10}(v/v_1)$ is plotted against $(x-x_1)$, as shown by full lines, for the values of x_1 indicated by the numbers on the lines and several values of K. The broken lines show the corresponding plots which would be

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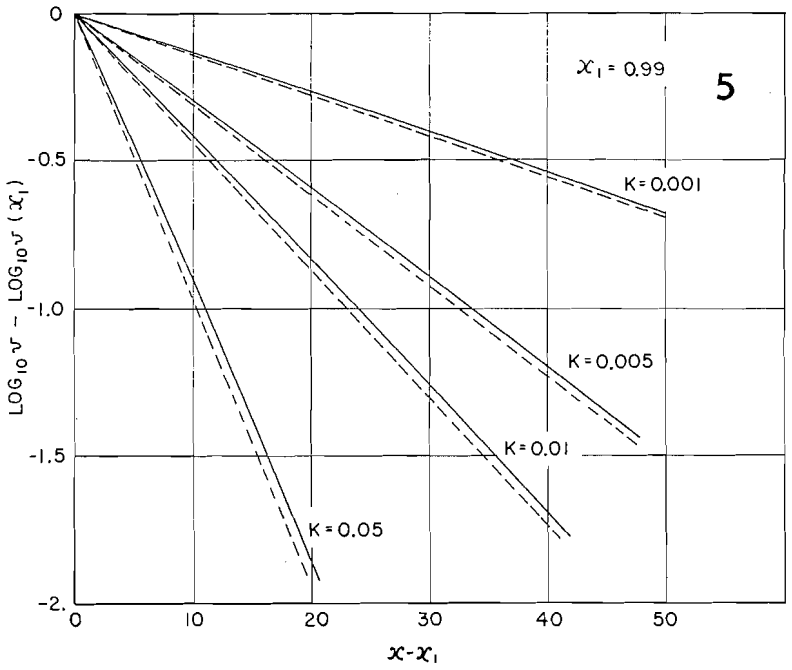

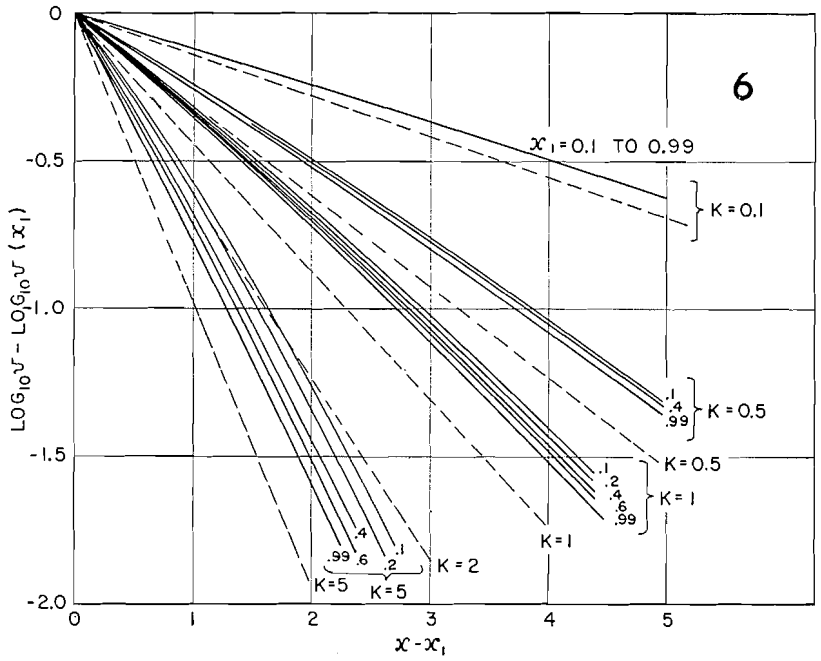

FIG. 5. Log(v/v_1) plots.
FIG. 6. Log(v/v_1) plots.

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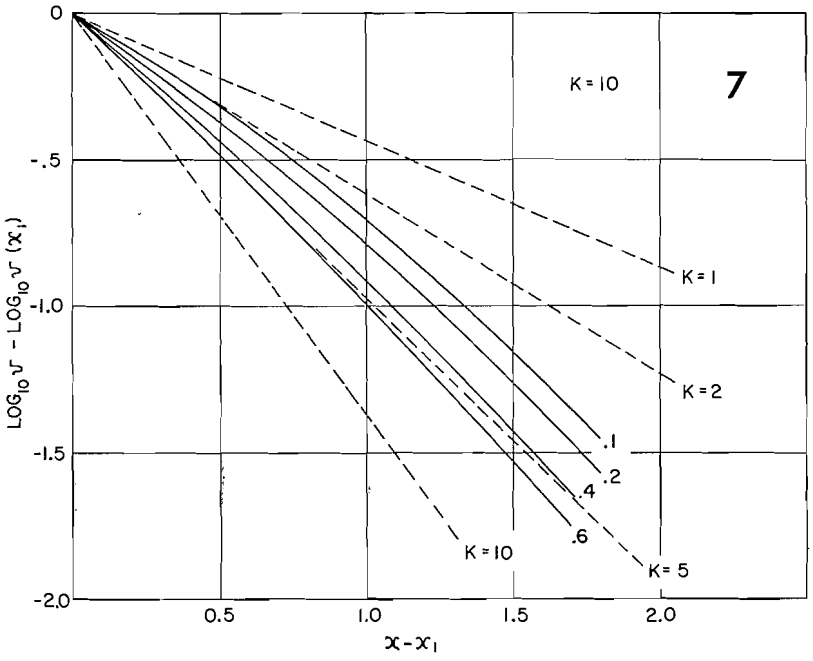

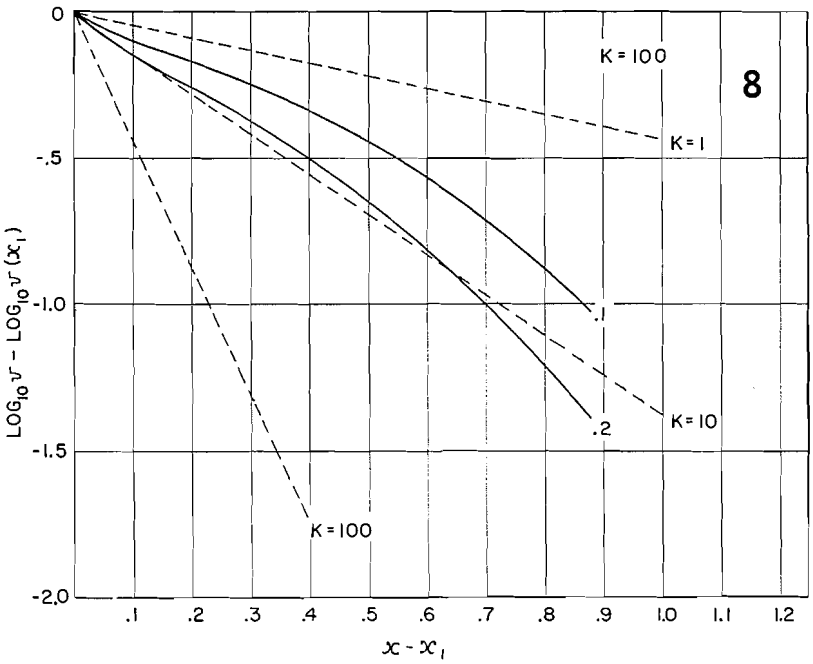

FIG. 7. $\text{Log}(v/v_1)$ plots.
FIG. 8. $\text{Log}(v/v_1)$ plots.

obtained for different values of K provided the exponential solutions were valid. The deviations can be estimated by comparing the slopes, since the ratio of the slopes is equal to the square root of the ratio of the corresponding rate constants.

DISCUSSION

Deviations in the Hartel–Polanyi Method (The Two-point Boundary Method)

From their definition it is evident that the quantities K and x_1 under the usual experimental conditions will vary as the value of the rate constant varies. With increasing speed of the reaction K will in general increase and x_1 decrease. It is clear from Figs. 1–4 and Table I that the deviation factor differs appreciably from unity even for quite slow reactions and becomes large for very fast reactions. Furthermore, for larger v_2/v_1 ratios, which correspond to smaller "flames", the deviation is greater. These results confirm the previous intuitive qualitative conclusions. In addition, since K becomes smaller for smaller r_1, the deviation is also decreased, showing that not only the r_2/r_1 ratio is of significance but also the absolute value of r_1.

The so-called "core" flames (4) are readily qualitatively explainable in terms of the present results, although the published data are not sufficiently detailed to allow a quantitative treatment. Inasmuch as r_1 and y_1 are independent of pressure variations in the reaction zone, the values of k_p should remain also pressure independent. The "core" flames, however, were characterized by a large pressure dependence of the calculated values of k_p, this dependence being more pronounced for faster reactions. In view of variation of D_y with pressure, z_∞ has also to be varied to maintain the flame size and as a result x_1 and therefore also K will be altered leading, in turn, to a drift in the values of δ and of k_p. With increasing pressure, D_y becomes smaller and, therefore, z_∞ is also reduced (for the same C) making x_1 smaller and K larger, and as a result k_p will decrease. This will be noticeable in the case of very fast reactions when x_1 is small and quite sensitive to variations in z_∞ and when δ is large. A change in experimental conditions leading to an increase in x_1 (and a decrease in K and δ) will tend to reduce the pressure dependence. These conclusions are in agreement with the drifts observed by Haresnape, Stevels, and Warhurst (4) and with the necessary change in experimental conditions intuitively inferred by these authors in order to eliminate the pressure dependence of k_p.

Deviations in the Concentration Pattern Method

The deviations from the exponential solution in the concentration pattern method are shown in Figs. 5–8. It is evident that they are on the whole considerably smaller than in the two-point boundary method and for a considerable range of experimental conditions they are practically negligible. This result is in agreement with the view expressed by Smith (8). Only for some quite large values of K the deviations could become appreciable. In this case, the evaluated rate constants would appear smaller than they actually are, and any pressure dependence would be such that with an increasing pressure the rate constants evaluated to the exponential approximation would decrease. Here

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again the smaller the absolute value of r_1 the smaller is K, and, consequently also the deviations. The necessity of selection of very small nozzle radii in the experiments of Garvin and Kistiakowsky (3) is, thus, well understandable.

Evaluation of r_1 and y_1

The solutions [8] are independent of the particular values which r_1 and y_1 may have and the foregoing results are, therefore, quite general. However, the constant A_p in Equation [2] which involves r_1 and y_1 has to be known for the calculation of k_p. The value of r_1 is also required for the quantitative evaluation of the deviation factor δ and of eventual deviations in the concentration pattern method.

Two distinct ways of assessing the values of these quantities have been suggested. Hartel and Polanyi (5) assumed that $r_1 = r_n$, where r_n is the radius of the nozzle, and $y_1 = y_n = y_s$, where y_s and y_n are the respective concentrations of the nozzle reactant in the saturator and in the nozzle. Hartel–Polanyi's boundary condition at the origin was used exclusively until very recently when Garvin and Kistiakowsky (3) proposed to assess the value of A_p by setting the consumption of the nozzle reactant in the reaction zone equal to the strength of the assumed point source of this reactant (expressed as the quantity introduced in unit time). Garvin–Kistiakowsky's boundary condition has been used further by Reed and Rabinovitch (7) and by Smith (8). The respective values derived by these authors differ somewhat between themselves. The treatment given by Smith is of particular interest since it is based on the extended theory of spherical diffusion (1) and takes into account the depletion of the atmosphere reactant. It leads to the results

$$[11] \qquad r_1 = \frac{v_n r_n^2}{4D_z}, \qquad y_1 = y_n \frac{D_z}{D_y}, \qquad A_p = \frac{v_n r_n^2}{4D_y} y_n \exp(C_p r_1),^*$$

where v_n is the streaming velocity of the gases in the nozzle.

The introduction of Garvin–Kistiakowsky's boundary condition and the subsequent work by Reed and Rabinovitch and by Smith represent a highly interesting new approach. At the same time, the importance of the distorting effect of the stream of the carrier gas leaving the nozzle, which tends to keep z away from the nozzle, is not yet fully understood. Smith thus proposes also an alternative way of normalizing the exponential solution (the first approximation of the general solution) to allow for the fact that depletion of y by reaction is insignificant inside some radius *not smaller* than r_n because of the effect of the jet. It is also likely that the physical conditions at the nozzle impose some upper limits on y_1 and r_1, such as $y_1 \leqslant y_n$ and $r_1 \leqslant r_n$, since at sufficiently high v_n a transition to "cylindrical flames" takes place. In view of this, it is possible that in much of the classical diffusion flame work, where larger nozzle radii were employed, the Hartel–Polanyi boundary conditions were valid to a good approximation. Use of smaller nozzle radii offers the advan-

**In the original treatment the factor ¼ appears to have been omitted accidentally and this value is given as $(v_n r_n^2/D_y)\, y_n \exp(C_p r_1)$. The value for y_1 is not given explicitly.*

tage of smaller deviations from the exponential solution and may be preferable for that reason and because of a smaller interference with the assumed rigorously spherical symmetry. The effect of a variation of the nozzle radius, however, ought to be subjected to a critical experimental study on the basis of the foregoing conceptions. The concentration pattern method, on the other hand, is largely free from any uncertainties and, inasmuch as it may prove experimentally feasible to extend it to sodium atom reactions by a suitable modification of the optical method, it could provide a valuable variant of the classical technique.

While the computations reported in the present article were in progress, Smith (8) succeeded in solving in terms of a tabulated function by successive approximations the second order non-linear differential equation of spherical diffusion derived by Cvetanović and LeRoy (1). In the region of its convergence the series representing this solution should yield results identical with the present after allowance is made for the particular boundary conditions adopted by this author.

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THE PARTIAL SEPARATION OF Na^{22} FROM Na^{24} BY ION EXCHANGE CHROMATOGRAPHY[1]

By R. H. Betts, W. E. Harris,[2] and Margaret D. Stevenson

ABSTRACT

Mixtures of the radionuclides Na^{22} and Na^{24}, as the chloride salts, have been partially separated by chromatographic methods. A column 102 cm. in length containing the cation exchange resin Dowex 50 was used. The eluant was 0.7 *M* hydrochloric acid. Na^{22} is held more strongly by the resin than is Na^{24}. The most effective separations were obtained at 25°C. and 5.5°C.; experiments at 48°C. and 68°C. showed much smaller isotope effects.

INTRODUCTION

The separation of isotopes by ion exchange chromatography was first demonstrated by Taylor and Urey in 1938 (15). These workers obtained partial separation of Li^6 from Li^7, and K^{39} from K^{41}, by elution from a column 30 ft. in length. A naturally occurring zeolite was used as an ion exchange material. Subsequently, partial separations of Li^6 from Li^7 and Ca^{40} from Ca^{45} have been obtained by other workers with synthetic cation exchange resins (7, 9, 11). Very recently, a note has appeared describing the separation of nitrogen isotopes by elution of NH_4^+ from a column of Dowex 50 effectively 600 ft. in length (13). In this work, the nitrogen in the trailing edge of the elution band contained 74% N^{15}; the ratio N^{15}/N^{14} in the starting material was 0.365%, i.e. the natural abundance ratio. This is a very striking result.

In the present work we report experiments relating to the partial separation of 2.7 yr. Na^{22} from 15.0 hr. Na^{24} using the cation exchange resin Dowex 50. This system was chosen for study because the 9% difference in mass between Na^{22} and Na^{24} made it a priori a particularly favorable case in which to observe isotopic separation. An added attractive feature of this isotope pair is that the ratio of Na^{24} to Na^{22} in a given solution can be determined very precisely by radiochemical methods. This technique was in fact used earlier in an unsuccessful attempt to separate these nuclides by elution with ammonium citrate from a 207 cm. Dowex 50 column (4).

Our choice of experimental conditions was based on the following considerations: (i) Sodium ion in aqueous solution does not form complexes with any known anion; there appeared to be no advantage, therefore, in using such eluting agents as citrate or lactate, which have been used with marked success in separating adjacent lanthanide or actinide elements. (ii) Hydrochloric acid was chosen as the eluant mainly because of its experimental convenience. The particular concentration used (0.7 *M*) was chosen to give a K_D of about 8. (K_D is a dimensionless quantity given by the ratio: moles Na^+ per gram of resin/moles Na^+ per gram of solution, and describes the equilibrium distribution of sodium ion between the resin and the liquid phase.) A theoretical

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analysis by Glueckauf (6) shows that for the size of resin particle used in the present work, increases in K_D beyond 8 or 10 have very little effect on the efficiency of the separation obtained. (iii) The flow rates chosen were in general the maximum which could be used while maintaining the column under near equilibrium conditions. Our criterion here was the shape of the elution curve; excessively high flow rates gave a markedly asymmetrical elution curve with a long tail. We have also made use of a theoretical analysis of this aspect (6) which indicated that the flow rates chosen were sufficiently low to obtain maximum efficiency of separation. (iv) The particle size of the resin has a profound effect on the separation achieved by a given length of column, maximum efficiency being obtained with minimum particle diameter. In this work we have used resin with the smallest available particle size.

EXPERIMENTAL

The resin used was 240–400 mesh Dowex 50 in the hydrogen form. After a preliminary purification (1), a small fraction of more uniform size was separated by elutriation with water. The average diameter of particles of this fraction was 25 microns, with 90% in the range 20 to 40 microns. The air dried resin had a capacity of 3.54 meq. of exchangeable hydrogen per gram.

The column was a Pyrex tube 0.90 cm. I.D., 107 cm. in length. It was jacketed with a second column, through which water at the required temperature was circulated from a constant temperature reservoir. The bottom of the column was sealed to a short capillary tube, without stopcock, to minimize dead space between the end of the resin bed and the exit from the column. The column, when operating, contained 36 gm. of resin in 102 cm., and 44 ml. of hydrochloric acid. The top 5 cm. was left free of resin to allow the eluting agent to attain the required temperature before it reached the top of the resin bed. Before each experiment, the resin was conditioned for one day by elution with 0.7 *M* hydrochloric acid.

Na^{22} was supplied as $Na^{22}Cl$ in dilute hydrochloric acid through the courtesy of Mr. R. C. Hawkings of these laboratories. It was purified before use by elution with dilute acid from a separate 60-cm. column of Dowex 50. The specific activity of this material was 25 μc. per mgm. of Na^{23}, i.e., $\sim 4 \times 10^{-4}$ atom % Na^{22}.

Na^{24} was prepared by irradiation of 1 mgm. quantities of analytical reagent sodium carbonate in the Chalk River NRX reactor. It was converted to $Na^{24}Cl$ by evaporation with dilute hydrochloric acid. The specific activity at the start of an experiment was about 2 mc. per mgm. of Na^{23}, corresponding to 2×10^{-5} atom % Na^{24}.

The eluant, 0.7 *M* hydrochloric acid, was prepared by dilution of reagent grade acid with doubly distilled water.

Procedure

Solutions of $Na^{22}Cl$ and $Na^{24}Cl$ were mixed in the required proportions, and the mixture evaporated to dryness twice with dilute hydrochloric acid to ensure that the two radionuclides were in equivalent chemical form initially.

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The resulting residue (which amounted to about 3 mgm. of sodium chloride) was dissolved in water, and a portion set aside for later analysis. The remainder was adsorbed on 0.2 gm. of resin, and the resultant slurry transferred to the top of the column. When this added resin had settled in a thin layer, the supernatant water was replaced with 0.7 *M* hydrochloric acid, and the top of the column connected to an overhead reservoir of eluant. The rate of flow of liquid through the column was maintained constant to ±5% by applying a suitable hydrostatic pressure to the top of the column. Provision was made for removing dissolved air from the acid before it entered the column.

Up to 40 consecutive fractions of effluent containing sodium were collected. Samples were prepared from these fractions for measurement of the relative isotopic ratio Na^{24}/Na^{22} (see below). For fractions very close to either end of the elution band, 15–20 ml. of solution were used to obtain a sufficient amount of activity. This volume was evaporated to dryness and most of the sodium removed from the traces of resin left behind by extraction with small volumes of water. Finally this aqueous extract was evaporated in a central depression on a copper tray. For most of the fractions, this preliminary concentration was unnecessary, and 0.05–0.5 ml. samples were evaporated directly on the copper trays.

Estimation of the Relative Na^{24}/Na^{22} Atom Ratio

The method used depends on measurement of the disintegration rate of a sample when both nuclides contribute about equally to the observed activity, followed by a second measurement after most of the Na^{24} had decayed, leaving only Na^{22} activity. It may be useful to point out here that the initial value of the atom ratio Na^{24}/Na^{22} in each run has no "natural" value, and moreover, in a given solution containing these nuclides, this ratio decreases by a factor of two every 15.04 hr. Nevertheless, for any sample this ratio may be given a definite value *referred to a fixed time*. In the following we measure not the absolute atom ratio, but a quantity which is directly proportional to it, viz., the ratio of counts per minute (c.p.m.) from Na^{24} to the corresponding quantity for Na^{22}. We define this ratio as N^{24}/N^{22}.

The relative radioactivity of each sample was measured in a fixed and reproducible geometrical arrangement with a 3 in. NaI–Tl crystal scintillator, coupled optically to a photomultiplier tube (RCA-5819). The crystal and photomultiplier were mounted inside 3 in. of lead shielding. The output from the tube was fed into a scaling circuit and mechanical register. After the Na^{24} in the sample had decayed to about 1% or less of its initial activity, the sample was remeasured.

The method of calculation of the relative isotopic ratio from such data is illustrated below.

At time T_1 let N_1 be the observed c.p.m. for a given sample. Then $N_1 = N_1^{24}+N_1^{22}$, where N_1^{24} and N_1^{22} are the c.p.m. in the sample arising from Na^{24} and Na^{22}, respectively.

Similarly, at time T_2:

$$N_2 = N_2^{24}+N_2^{22}.$$

Since the half-life of Na^{22} is long relative to periods of time dealt with here, then

$$N_1^{22} \simeq N_2^{22},$$

and
$$\Delta N = N_1 - N_2 = N_1^{24} - N_2^{24}$$
$$= N_2^{24}\,[\exp(0.693\,\Delta T/15.04) - 1],$$

where ΔT (in hours) $= T_1 - T_2$, and 15.04 is the half-life of Na^{24} in hours (10).

If we let
$$\exp(0.693\,\Delta T/15.04) = f,$$

then
$$N_2^{24} = \Delta N/(f-1),$$

and

[1]
$$\frac{N_1^{24}}{N_1^{22}} = \frac{N_1 - N_2 + [\Delta N/(f-1)]}{N_2 - [\Delta N/(f-1)]},$$

which is the required result.

Since $(f-1)$ was generally of the order of 80 to 300 (ΔT = 95 to 125 hr.), the terms in f in Equation [1] represent small corrections to this ratio.

Finally, N_1^{24} for each sample in a run was adjusted to some common time in the vicinity of T_1 in the usual way. For this purpose, the half-life of Na^{24} was taken as 15.04 hr. (10).

In the foregoing we neglected the radioactive decay of Na^{22} which occurred during the time ΔT (4–6 days). While this procedure would lead to a 0.3 to 0.4% error in the calculation of *absolute* isotopic abundance, these errors cancel in the present case, since we are interested only in variations in the relative abundance among different samples for which ΔT was effectively constant.

Precision of the Measurement of N^{24}/N^{22}

As will be apparent from the results presented later, a maximum variation of 10% was observed in the ratio N^{24}/N^{22} between the leading and trailing edges of the sodium elution curve in a given run. We feel therefore that it is necessary to outline in rather more detail than is customary further particulars of the counting techniques used, and the precautions taken to minimize errors.

A sufficient number of counts were recorded for each sample to reduce the probable statistical error in the ratio N^{24}/N^{22} to $\pm 0.2\%$. Corrections were made when required for variations in the counting rate of a standard sample (Na^{22}) and for background. Coincidence corrections were applied when necessary. To make this latter correction, the dead time of the counter was measured with paired sources (5, p. 213) of both Na^{22} and Na^{24}, at counting rates comparable with those encountered in the present work. Systematic errors arising from uncertainties in the dead time were minimized by preparing, whenever possible, all comparable sources with nearly equal counting rates. To further reduce the effects of drifts in the counting equipment, the samples in each run were measured in a random progression, viz., the chronological order of counting the samples did not correspond to the order in which these samples came off the column. In addition, samples of the initial solution were measured at irregular intervals during the time in which the samples of effluent from the column were being assayed. Such a procedure served as a secondary "internal" standard to the whole scheme of radioassay.

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Since a ratio of counting rates at two times for a given sample is involved, the precision of the method is unaffected by pipetting errors, and more generally does not depend on quantitative transfers at any stage of sample preparation. For the same reason, errors due to slight variations in geometry from one sample to another are also mainly self-cancelling. Errors arising from variable self-absorption in the sources were also negligible because the counting arrangement responded only to γ-rays. In any event, the sources were essentially weightless.

As a measure of the reproducibility of the counting technique, we record below (Table I) typical results for the ratio N^{24}/N^{22} for triplicate samples of the initial solutions in each of three experiments.

TABLE I

VALUES OF N^{24}/N^{22} FOR TYPICAL STOCK SOLUTIONS

Sample No.	Run No.		
	11	12	13
1	1.227	1.889	4.245
2	1.228	1.884	4.251
3	1.230	1.885	4.233
Average	1.228 ± 0.001	1.886 ± 0.003	$4.24_3\pm0.007$

Another more general test of the counting methods was to assay a series of synthetic mixtures of $Na^{22}+Na^{24}$ which were prepared by mixing together weighed portions of solutions of each of these nuclides. A comparison of the observed and calculated values of the ratio N^{24}/N^{22} for these mixtures is given in Table II.

TABLE II

MEASUREMENTS OF N^{24}/N^{22} FOR SYNTHETIC SOLUTIONS

Solution No.	N^{24}/N^{22}	
	Obs.*	Calc.
1	0.980 ± 0.003	0.979
2	0.996 ± 0.002	0.994
3	1.023 ± 0.003	1.019
4	1.035 ± 0.003	1.039
5	1.055 ± 0.003	(1.055)†
6	1.074 ± 0.002	1.072

*Average of two values.
†Fitted value.

The results in Tables I and II suggest that the probable error in estimation of N^{24}/N^{22} does not exceed $\pm0.4\%$.

RESULTS

1. *General Features of the Elution of Sodium Ion*

Fig. 1 is a typical elution curve obtained in this work. This result is for Run 13 at 24.8°C. (See Tables III and V below.) The elution curves for other runs did not differ markedly from that shown in Fig. 1, although the curves

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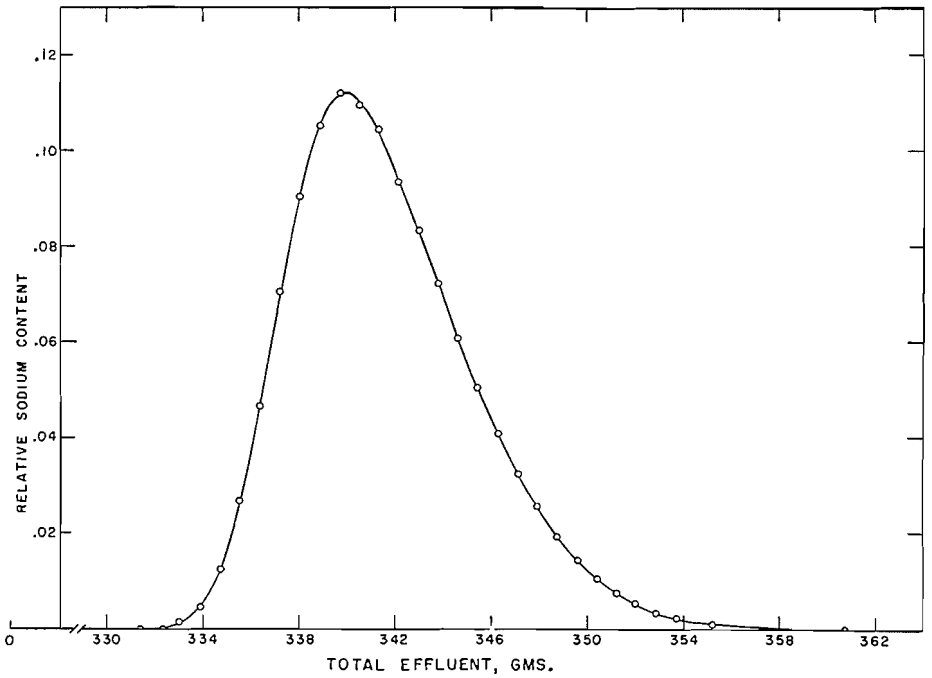

FIG. 1. Sodium elution curve for Run 13 at 24.8°C.

obtained at 5.5°C. showed a longer tail than those at higher temperatures. The position of the maximum decreased with increases in temperature, occurring at 400±5 gm. of eluant at 5.5°C., and at 290 gm. at 67.8°C. These shifts in position of the maximum are presumably caused by corresponding changes in the distribution coefficient of sodium ion between resin and solution. The magnitude of the change agrees with other measurements in the literature on the enthalpy change associated with the sodium–hydrogen exchange on Dowex 50 (3).

It was thought of interest, in passing, to calculate by standard methods (12, p. 190) the number of theoretical plates in the column. The position and width of the elution curve shown in Fig. 1 leads to a value of 10,000 theoretical plates, i.e., 100 per cm. of column length. For comparison, calculations based on physical parameters like particle size, flow rate, etc., according to Glueckauf's treatment of ion exchange chromatography (6) gave a value of 218 plates per cm. In a private communication, Glueckauf and Kitt (8) suggest that allowance should be made in the latter calculation for "wall" effects which cause a curvature in the advancing boundary of the elution band. Their experimental studies of this phenomenon point to a value of 100 to 120 plates per cm. for the flow rate and particle size used in the present study. This is in good agreement with the experimental value of 100 plates per cm. quoted above.

2. *Separation of Na^{24} from Na^{22}*

Table III summarizes the main results of the present investigation. The items listed are self-explanatory, except for (i) "$(N^{24}/N^{22})_{total}$ in effluent" and

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(ii) "Maximum separation, %". With respect to (i), the c.p.m. of Na^{22} and of Na^{24} in each fraction were calculated from the volume of the fraction, the total activity per ml., and the measured ratio N^{24}/N^{22} for each fraction. The total amount of both Na^{24} and Na^{22} in the effluent as a whole was calculated from these data. The ratio of these amounts is designated as $(N^{24}/N^{22})_{total}$ in Table III. The value of this ratio for each run agrees with N^{24}/N^{22} determined on aliquot portions of the corresponding stock solution before its passage down the column. This agreement is a further check on the experimental procedures, and, in addition, is indirect evidence that radioactive nuclides other than Na^{22} and Na^{24} were absent in the stock solutions. The "maximum separation" (ii) referred to in Table III was calculated from

$$\frac{(N^{24}/N^{22})_{max} - (N^{24}/N^{22})_{min}}{(N^{24}/N^{22})_{stock}} \times 100\%.$$

Table III shows that at 5.5°C. and 25°C., significant enrichment of Na^{24} occurred in the leading fractions, and depletion of Na^{24} in the trailing fractions. The separation of Na^{22} from Na^{24} is unquestionably less at 48° and 68°C., and may well be zero.

TABLE III

SUMMARY OF DATA

	Run No.							
	9	10	11	12	13	5	4	8
Temperature, °C.	5.5	5.5	5.5	5.5	24.8	24.9	48.4	67.8
Flow rate, gm./min.	0.11	0.055	0.11	0.10	0.14	0.15	0.27	0.10
N^{24}/N^{22} stock solution*	2.318	0.496	1.228	1.886	4.24	6.44	5.35	4.68
$(N^{24}/N^{22})_{total}$ in effluent	2.33	0.495	1.219	1.884	4.24	6.41	5.35	—
Maximum N^{24}/N^{22}, leading fraction	2.40	0.510	1.290	1.975	4.43	6.72	5.38	4.70
Minimum N^{24}/N^{22}, trailing fraction	2.15	0.461	1.190	1.824	4.09	6.27	5.25	4.53
Maximum separation, %	10	10	8	8	8	7	2	3

**Average of three values.*

To amplify the results in Table III, we list in Tables IV and V the relative isotopic analyses for all samples collected in each of two experiments. These tables show that the central fractions, corresponding to those near the peak in Fig. 1, emerge from the column essentially unchanged in isotopic composition. Only the leading and trailing fractions show significant changes in the atom ratios.*

**The slight rise in N^{24}/N^{22} in the last 0.5 to 1% eluted, shown in Table IV, was noted in several other runs, particularly those at 5.5°C. We believe this effect could arise, for example, by adsorption of traces of sodium on the glass surfaces of the column, followed by a slow removal by the eluting agent. Such effects would tend to cancel any isotopic separation. Similar behavior has been observed in the separation of americium from curium. These elements appear in the effluent in two distinct, well-separated peaks; nevertheless, the last 1 to 2% of material eluted contains both americium and curium (2).*

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TABLE IV

DATA FOR RUN 12 AT 5.5°C.

Initial $N^{24}/N^{22} = 1.886 \pm 0.003$ (see Table I)

Fraction Na eluted	N^{24}/N^{22}	Fraction Na eluted	N^{24}/N^{22}
0–0.0018	1.975	0.774–0.810	1.858
0.0018–0.0059	1.966	0.810–0.842	1.845
0.0059–0.0191	1.941	0.842–0.869	1.851
0.0191–0.045	1.933	0.869–0.892	1.834
0.045 –0.088	1.930	0.892–0.911	1.828
0.088 –0.146	1.927	0.911–0.928	1.841
0.146 –0.216	1.917	0.928–0.941	1.824
0.216 –0.292	1.902	0.941–0.953	1.820
0.292 –0.369	1.899	0.953–0.960	1.842
0.369 –0.442	1.888	0.960–0.967	1.832
0.442 –0.513	1.892	0.967–0.976	1.831
0.513 –0.576	1.878	0.976–0.982	1.838
0.576 –0.635	1.877	0.982–0.989	1.838
0.635 –0.687	1.885	0.989–0.996	1.862
0.687 –0.734	1.853	0.996–0.998	1.873
0.734 –0.774	1.849	0.998–1.000	1.870

TABLE V

DATA FOR RUN 13 AT 24.8°C.

Initial $N^{24}/N^{22} = 4.243 \pm 0.007$ (see Table I)

Fraction Na eluted	N^{24}/N^{22}	Fraction Na eluted	N^{24}/N^{22}
0. –0.0004	4.433	0.770–0.821	4.213
0.0004–0.0017	4.422	0.821–0.862	4.190
0.0017–0.0056	4.370	0.862–0.896	4.177
0.0056–0.016	4.356	0.896–0.923	4.176
0.016 –0.038	4.347	0.923–0.944	4.140
0.038 –0.077	4.310	0.944–0.960	4.144
0.077 –0.135	4.306	0.960–0.972	4.154
0.135 –0.209	4.312	0.972–0.981	4.119
0.209 –0.296	4.296	0.981–0.987	4.092
0.296 –0.388	4.266	0.987–0.992	4.099
0.388 –0.479	4.251	0.992–0.994	4.129
0.479 –0.565	4.236	0.994–0.996	4.111
0.565 –0.642	4.222	0.996–0.999	4.108
0.642 –0.711	4.215	0.999–1.000	4.133
0.711 –0.770	4.221		

A useful way of displaying such results is to plot $\Sigma Na^{24}/\Sigma Na^{22}$ vs. % elution of sodium. The Σ refers to the cumulative fraction of Na^{24} or Na^{22} in the effluent from the beginning of the elution. Fig. 2 shows such plots for several runs. The meaning of these curves is best illustrated by example. In Runs 11 and 12 (upper curve in Fig. 2), an enrichment of 1.4% in Na^{24} relative to Na^{22} would be obtained by collecting the first 50% of the effluent, and a 2.6% enrichment if the first 10% of the sodium is collected. Successively higher enrichments are obtained as the % of total sodium eluted approaches a value of zero.

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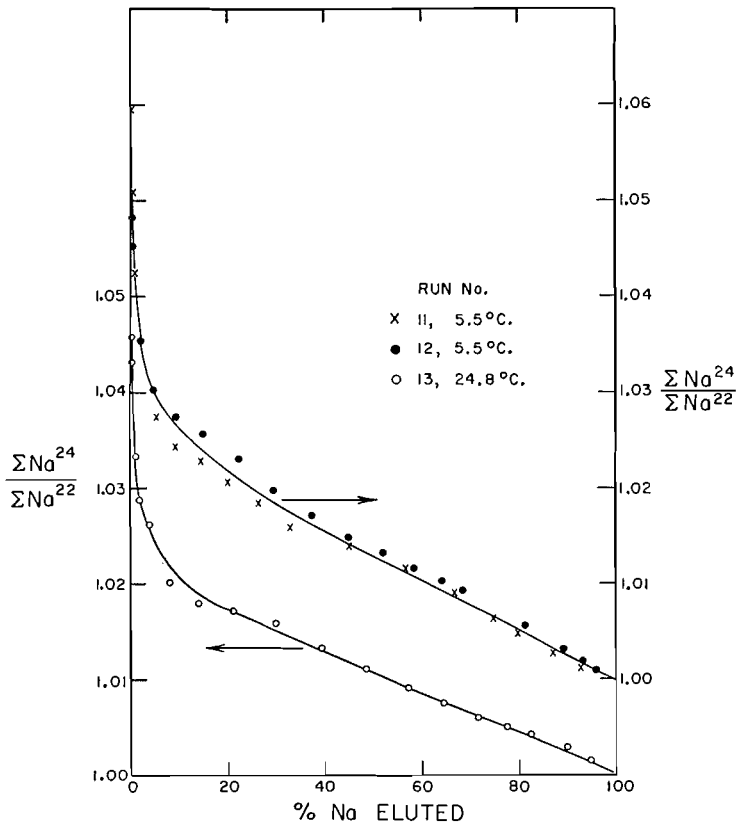

FIG. 2. Enrichment of effluent in Na^{24}.

DISCUSSION

An analysis of the results at 5.5°C. indicates that the peak of the Na^{24} curve is reached about 0.05 to 0.07 ml. earlier than the peak for Na^{22}. If the observed separation is ascribed solely to differences in K_D between the two nuclides, then this result implies that K_D for Na^{24} is 1 part in 6000 smaller than K_D for Na^{22}. This small difference presumably represents the net result of isotope effects on at least two equilibria: (i) the interaction of sodium ion with water molecules of the hydration sphere, and (ii) the reaction of the hydrated ion with the resin. In this connection it is pertinent to note that experiments with H_2O^{16}–H_2O^{18} mixtures have revealed isotope effects in the hydration of chromium (III) and certain other cations (14).

A further point of interest is the virtual absence of separation at 48° and 68°C. The distribution of sodium ion between the resin and acid is not markedly temperature sensitive (3); it is unlikely, therefore, that the difference in the temperature coefficients for the distribution of these nuclides would be sufficiently large to cancel out the isotope effect at 48°C., when it is clearly observable at 5° and 25°C. This absence of separation at higher temperatures may be due to convective mixing of the elution band due to slight temperature

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gradients in the system, or possibly to mixing caused by formation of bubbles at these temperatures. Although, as indicated earlier, precautions were taken to reduce such effects, further work with more careful attention to these points would be desirable.

A comparison of the present results with those referred to earlier (7, 9, 11, 13, 15) shows that on Dowex 50 the heavier nuclide is less firmly held by the resin for the pairs Li^6–Li^7 and Na^{22}–Na^{24}. The behavior of N^{14}–N^{15} is reversed, N^{15} being more strongly retained by the resin than is N^{14}. While perhaps not strictly comparable, the separation of K^{39} from K^{41} obtained with zeolitic (inorganic) material showed that the lighter isotope comes off the column first (15). The same trend is evident for the Ca^{40}–Ca^{45} separations, i.e., the lighter nuclide comes off the column preferentially (11). This result is also probably not comparable with the lithium and sodium studies, since a complexing agent (ammonium citrate) was used as an eluting agent. However it is clear that the order of elution of members of isotopic pairs in the mass range 6 to 45 is not a simple function of the relative masses of the nuclides involved. Further studies of other isotopic pairs above calcium, e.g., Fe^{56}–Fe^{59}, would be useful in this connection. Parallel studies of isotope effects concerned in complex ion formation would also be instructive.

ACKNOWLEDGMENTS

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AN ISOTOPIC STUDY OF THE REDUCING ACTION OF THE GRIGNARD REAGENT[1]

By G. E. Dunn and John Warkentin[2]

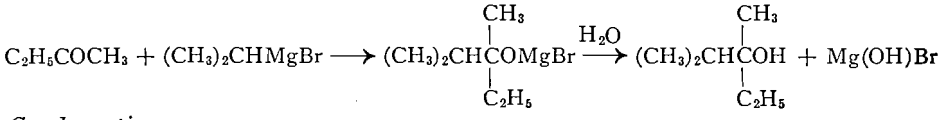
ABSTRACT

Benzophenone has been reduced to benzhydrol with three samples of isobutylmagnesium bromide containing deuterium in the *alpha*, *beta*, and *gamma* positions, respectively. Deuterium was found only in the benzhydrol obtained from β-deuteroisobutylmagnesium bromide. Comparison of the ratios of deuterium to protium in β-deuteroisobutylmagnesium bromide and in the benzhydrol obtained from it shows an isotope effect of about two. In the decarboxylation of hydroxyl-deuterated dimethylmalonic acid an isotope effect of 4.5 was observed. These results are considered in terms of the probable mechanisms of the reactions.

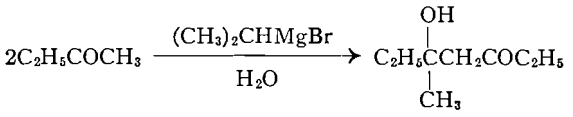
INTRODUCTION

Of the many reactions of the Grignard reagent, the most familiar and probably the most used is the addition to a carbonyl group. It has long been known, however, that this reaction is frequently complicated by side reactions which may replace some or all of the addition. The three most important of these side reactions are commonly referred to as condensation, enolization, and reduction (8). They are illustrated below in terms of methyl ethyl ketone and isopropylmagnesium bromide (15).

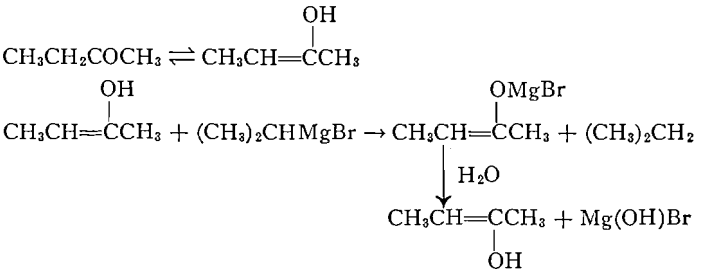
Addition



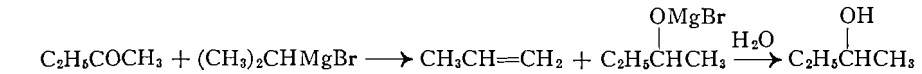
Condensation



Enolization



Reduction



[1]*Manuscript received September 12, 1955.*

Contribution from the Chemistry Department of the University of Manitoba, Winnipeg, Manitoba. This paper was presented at the May, 1955, meeting of the Chemical Institute of Canada at Quebec City, Quebec.

[2]*Holder of a National Research Council Bursary, 1954–55.*

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The condensation reaction is, at least formally, analogous to the common base-catalyzed aldol condensation with the Grignard reagent as the base, and the enolization reaction is an example of the well-known tendency of the Grignard reagent to react with acidic hydrogen. The reduction reaction, however, shows a property of the Grignard reagent which is not illustrated among its better known reactions and, consequently, this side reaction has attracted more interest and experiment than the other two.

The equation written above for the reduction reaction indicates that the Grignard reagent is converted into olefin, and careful work by Noller, Grebe, and Knox has shown that, at least in the reduction of benzophenone by isobutylmagnesium bromide, the amounts of olefin and alcohol produced are exactly equivalent (14). It is also commonly observed that the double bond of the olefin has for one of its carbon atoms that one to which magnesium was originally attached. For example, γ-phenylpropylmagnesium bromide when used as a reducing agent is converted into allylbenzene (2). Evidently the net result of the reaction is the elimination of magnesium and hydrogen from adjacent carbon atoms. This conclusion is supported by the observation that, although the amounts of all three side reactions increase with increasing branching in the alkyl groups of both carbonyl and Grignard reagents, reduction does not occur when the Grignard does not contain a hydrogen atom on the carbon *beta* to magnesium (20).

Although the evidence considered above shows that the over-all result of the reduction is the transfer of the elements of magnesium halohydride from Grignard reagent to carbonyl compound, it does not, of course, prove that a hydrogen atom originally attached to the β-carbon of the Grignard is the one actually transferred to the carbonyl compound. It is conceivable that the actual hydrogen atom appearing in the carbinol product could come from the α- or γ-position of the Grignard reagent, from the solvent, or from the water used in the hydrolysis. However, in the absence of evidence to the contrary, attempts to devise a mechanism for the reduction have naturally been based on the simplest reasonable assumption: namely, that a hydride ion is transferred directly from the Grignard molecule to the carbonyl compound.

The objects of the present investigation have been: first, by substituting deuterium for hydrogen in various positions of the Grignard molecule to determine whether or not the hydrogen atom lost from the β-position of the Grignard reagent is, in fact, the one which appears in the carbinol product of the reduction; and, second, by observing the isotope effect in the hydrogen transfer to learn something about the sequence and relative speeds of the various steps in the reaction.

The reaction we have chosen to study is the reduction of benzophenone to benzhydrol by isobutylmagnesium bromide:

$$(C_6H_5)_2CO + (CH_3)_2CHCH_2MgBr \rightarrow (CH_3)_2CH{=}CH_2 + (C_6H_5)_2CHOMgBr$$

$$\downarrow H_2O$$

$$(C_6H_5)_2CHOH + Mg(OH)Br$$

It was chosen for a number of reasons: (*a*) the ketone cannot undergo condensation or enolization and gives an almost quantitative yield of the reduction

product; (*b*) this reaction is one of the very few for which it has been demonstrated that the amounts of olefin and alcohol produced are equivalent; (*c*) the Grignard has hydrogen in the α-, β-, and γ-positions which could, in principle, be transferred to the ketone; and (*d*) the halomagnesium salt of benzhydrol is insoluble in ether so that it can readily be separated from unreacted benzophenone and other reaction products, if any.

Three samples of isobutylmagnesium bromide were prepared which contained deuterium in the α-, β-, and γ-positions respectively. Benzophenone was reduced by each of these, using two equivalents of Grignard reagent to one of benzophenone. By analyzing the resultant benzhydrol samples for deuterium it could be determined whether or not hydrogen is transferred from the Grignard reagent and, if so, from which position in it. By comparing the deuterium to protium ratios in the Grignard reagent and in the benzhydrol obtained from it the isotope effect in the reaction could be determined.

EXPERIMENTAL

The deuterated Grignard reagents required for this work were prepared from deuterated isobutyl bromides obtained from the corresponding deuterated isobutyl alcohols. A variety of methods for the synthesis of these alcohols were explored, using undeuterated materials. The yields quoted in the procedures described below are those obtained from the undeuterated materials since the small quantities of deuterated compounds used were usually distilled directly into the reaction vessel for the next step in the synthesis without measurement.

α-Deuteroisobutyl Alcohol

This compound was made by reduction of isobutyraldehyde with lithium aluminum deuteride. Isobutyraldehyde (4.2 gm., 0.058 mole) in 20 ml. of dry ether was added dropwise to a stirring solution of 0.65 gm. (0.017 mole) of lithium aluminum deuteride in 20 ml. of ether. A 45 min. reflux period was followed by hydrolysis with dilute hydrochloric acid and extraction of the aqueous layer with ether. The dried ether extracts were evaporated and the residue distilled. The yield of isobutyl alcohol boiling in the range 96–107°C. was 70%.

β-Deuteroisobutyl Alcohol

This compound was synthesized by the following series of reactions:

$$CH_3CH(COOEt)_2 \xrightarrow[CH_3I]{NaOEt} (CH_3)_2C(COOEt)_2 \xrightarrow{KOH} (CH_3)_2C(COOH)_2 \xrightarrow{D_2O} (CH_3)_2C(COOD)_2$$

$$(CH_3)_2C(COOD)_2 \xrightarrow[-CO_2]{heat} (CH_3)_2CDCOOD \xrightarrow{LiAlH_4} (CH_3)_2CDCH_2OH$$

Methylmalonic acid diethyl ester (26.0 gm., 0.16 mole) was added to a solution of 3.8 gm. of sodium (0.16 gm-atom) in 100 ml. of absolute ethanol. Then 22.7 gm. (0.16 mole) of methyl iodide was added dropwise. After a three-hour reflux period 2 ml. of methyl iodide was added and refluxing continued for another hour. Ethanol was distilled off and the residue treated with water.

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From ether extracts of the aqueous solution there was obtained 9.1 gm. of dimethylmalonic acid diethyl ester boiling at 186–190°C., a yield of 68%.

This ester was saponified by refluxing it for 2.5 hr. with an equal weight of potassium hydroxide dissolved in its own weight of water. Unsaponified ester was removed by extraction with ether. Dimethylmalonic acid was isolated by extracting the acidified aqueous solution with ether, evaporating the ether, and crystallizing the residue from benzene. It melted at 188–190°C. Yields were 90% or better. Recrystallization from ether raised the melting point to the literature value of 192–193°C. Neutral equivalent was 67.5±2.0 as compared to calculated values of 66 for dimethylmalonic acid and 59 for methylmalonic acid.

Dimethylmalonic acid (21.5 gm., 0.163 mole) was equilibrated with deuterium oxide by dissolving it in 60 ml. of dioxane (purified by the method of Fieser (4), containing 3.3 gm. (0.165 mole) of heavy water[3] and allowing the solution to stand at room temperature for 70 hr. Dioxane and water were removed at 90°C. under reduced pressure, and the residue of deuterodimethylmalonic acid was decarboxylated by heating the distilling flask containing it above 195°C. in an oil bath. The deuteroisobutyric acid which distilled over had a neutral equivalent of 91±2 compared to the calculated value of 89. The over-all yield of exchange and decarboxylation was 85%.

Deuteroisobutyric acid (12.0 gm., 0.14 mole) in 15 ml. of dry ether was added dropwise with stirring to a suspension of lithium aluminum hydride (7.0 gm., 0.14 mole) in 45 ml. of ether. The mixture was refluxed for an hour, then hydrolyzed with water, and acidified. From the ether layer was obtained 6.1 gm., a 60% yield, of β-deuteroisobutyl alcohol, b.p. 96–107°C.

γ-Deuteroisobutyl Alcohol

This compound was prepared by the following series of reactions:

$$(CH_3)_2CO \xrightarrow{D_2O} (CD_3)_2CO \xrightarrow{LiAlH_4} (CD_3)_2CHOH \xrightarrow{PBr_3} (CD_3)_2CHBr \xrightarrow{Mg}$$
$$(CD_3)_2CHMgBr \xrightarrow{CO_2} (CD_3)_2CHCOOH \xrightarrow{LiAlH_4} (CD_3)_2CHCH_2OH$$

Acetone (30 gm., 0.52 mole) was equilibrated with deuterium oxide (30 gm., 1.5 mole) containing 0.2 gm. of sodium hydroxide. After 48 hr. at room temperature the mixture was distilled through a 9×1.5 cm. column packed with 3 mm. glass helices, distillate being collected up to 95°C. This deuteroacetone was dried over calcium sulphate and filtered.

Deuteroacetone (14.0 gm., 0.24 mole) was dissolved in 20 ml. of dry diethyl carbitol and the solution was added slowly to a suspension of 3.0 gm. (0.08 mole) of lithium aluminum hydride in 20 ml. of diethyl carbitol. At the end of 1.5 hr. the mixture was acidified with dilute hydrochloric acid and distilled, distillate bieng collected up to 95°C. This distillate was redistilled through a 9×1.5 cm. column packed with 3 mm. glass helices. The yield of deuteroisopropyl alcohol boiling at 79–81°C. was 11.4 gm. (80%).

[3]*Heavy water was obtained from the Commercial Products Division of Atomic Energy of Canada, Ltd., and was reported by the supplier to contain 99.73 atom-% deuterium.*

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Deuteroisopropyl alcohol was converted to the corresponding bromide, b.p. 56–60°C., in 55% yield by the method described below for converting deuteroisobutyl alcohol to its bromide.

Deuteroisopropyl bromide (24.5 gm., 0.20 mole) was converted to the Grignard reagent with 0.22 gm-atom of magnesium in 60 ml. of dry ether in the usual way. The yield by titration with standard acid was 85%. This was poured into a slurry of crushed Dry Ice in ether; the mixture was acidified and extracted with ether. From the ether extracts was obtained 11.6 gm. (78%) of deuteroisobutyric acid boiling at 145–150°C.

Deuteroisobutyric acid was reduced to γ-deuteroisobutyl alcohol by means of lithium aluminum hydride in ether as described above under β-deuteroisobutyl alcohol. The yield was 65%.

Conversion of Deuteroisobutyl Alcohols to Deuteroisobutyl Bromides

Phosphorus tribromide (19.5 gm., 0.072 mole) was added dropwise with stirring to 12.8 gm. (0.173 mole) of isobutyl alcohol over a period of 45 min. while the reaction was being cooled in an ice–salt bath. The mixture was then distilled, distillate being collected up to 96°C. This distillate was cooled to 0°C., washed with cold concentrated sulphuric acid, cold sodium carbonate solution, and cold water in turn, then dried and distilled. Yields of the various deuterated isobutyl bromides boiling at 88–92°C. ranged from 40% to 50%.

Reduction of Benzophenone by Deuterated Grignard Reagents

The three deuterated isobutyl bromides obtained from the above reactions were diluted with ordinary isobutyl bromide where necessary to give enough material for the subsequent reductions, then analyzed for deuterium. Three reductions with each bromide were attempted. In a typical run 3.0 gm. (0.022 mole) of deuterated isobutyl bromide in 5 ml. of dry ether was added to a 10% excess of magnesium (0.53 gm.) in 25 ml. of dry ether. Reaction was initiated by gentle warming, and completed by refluxing for three hours. Titration with standard acid showed the yield to be 75%. To this solution was added slowly one-half of the equivalent quantity (1.51 gm., 0.0083 mole) of benzophenone dissolved in 10 ml. of dry ether. The solution turned deep red as soon as the ketone was added, but the color disappeared when the addition was complete and the solution had been refluxed for a few minutes. After a few hours of reflux, the bromomagnesium salt of benzhydrol was allowed to settle out, filtered, washed with ether, and hydrolyzed with dilute acid. The liberated benzhydrol was extracted with ether and recrystallized from ligroin. The yield of benzhydrol melting at 66°C. was 1.2 gm. (80%).

Deuterium Analyses

The samples were burned in a standard macrocombustion apparatus using a Vycor tube and a plug of silver wool to trap halogens. The water of combustion was collected in a Dry Ice trap and purified by the method of Keston, Rittenberg, and Schoenheimer (6) except that calcium oxide and potassium permanganate were used instead of chromium trioxide and potassium hydroxide. The density of the water of combustion was determined by the gradient

density tube method described by Anfinsen (1). Two gradients were used, one covering the range 0–8% D_2O for samples rich in deuterium and another covering the range 0–2% D_2O for less concentrated samples.

RESULTS

Table I lists the analytical results. The three runs with α-deuteroisobutyl bromide used the same starting material so that the three analyses of α-deuteroisobutyl bromide are, in effect, triplicate analyses of the same material. Thus the three analyses illustrate the reproducibility of the method.

TABLE I

DEUTERIUM ANALYSES

Source of water sample	Run No.	Weight-% D_2O*	Atom ratio D/H in labelled position
α-Deuteroisobutyl bromide	1	0.70	0.029
	2	0.68	0.028
	3	0.69	0.029
Benzhydrol from α-deuteroisobutyl bromide	1	0.00	0.000
	2	0.00	0.000
	3	0.00	0.000
β-Deuteroisobutyl bromide	1	1.38	0.126
	2	1.48	0.137
	3	—	—
Benzhydrol from β-deuteroisobutyl bromide	1	0.65	0.076
	2	0.78	0.092
	3	—	—
γ-Deuteroisobutyl bromide	1	20.65	0.397
	2	21.32	0.418
	3	—	—
Benzhydrol from γ-deuteroisobutyl bromide	1	0.00	0.000
	2	0.03	0.003
	3	0.00	0.000
α-Deuteroisobutyric acid (dimethylmalonic acid)	1	14.16	1.072
	2	14.41	1.109
	3	14.39	1.107
β-Deuteroisobutyl alcohol	1	3.06	0.382
	2	3.08	0.384
	3	—	—

**A blank space indicates that a run or analysis was lost by accident.*

It is seen from the table that the benzhydrols obtained by reduction of benzophenone with β-deuteroisobutyl Grignard reagents contain deuterium while those obtained from α- and γ-deutero Grignard reagents do not. Therefore, the reduction occurs by hydrogen transfer from the β-position of the Grignard reagent, as has long been supposed.

The fact that the ratio of deuterium to protium in the labelled position of the benzhydrol is less than that in the β-deuteroisobutyl bromide from which

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it was obtained indicates that there is an isotope effect in the transfer.[4] The numerical value of the isotope effect can be calculated from the following considerations. If the reaction is assumed to be first order with respect to Grignard reagent, then

$$k_H t = \ln [a/(a-x)] \quad \text{and} \quad k_D t = \ln [a'/(a'-x')]$$

are the rate expressions for the reactions of normal and deutero Grignard reagents, respectively, where k_H is the rate constant for the transfer of hydrogen, k_D is the rate constant for the transfer of deuterium, a is the initial concentration of non-deuterated Grignard, a' is the initial concentration of deuterated Grignard, x is the concentration of non-deuterated product at time t, and x' is the concentration of deuterated product at time t. The isotope effect, k_H/k_D, is then given by the expression

$$[1] \qquad \frac{k_H}{k_D} = \frac{\log[a/(a-x)]}{\log[a'/(a'-x')]}.$$

If the substitutions $a'/a = A$, $x'/x = X$, and $(x+x')/(a+a') = P$ are made, the above expression becomes

$$[2] \qquad \frac{k_H}{k_D} = \frac{\log(1+X)-\log[1+X-P(1+A)]}{\log(1+1/X)-\log[1+1/X-P(1+1/A)]}$$

where A is the ratio of deuterium to protium in the labelled position of the reactant, X is the ratio of deuterium to protium in the labelled position of the product, and P is the fraction of reaction completed.

Since purified benzhydrol was isolated corresponding to 80% or more of the benzophenone used in the reactions, it is evident that the reduction of benzophenone must have been close to quantitative. And since two equivalents of Grignard were used to one of benzophenone, the fraction of Grignard reacted is one-half. Using this value for P and the values of X and A from Table I, the isotope effect, k_H/k_D, is found to be 2.0 in Run 1, and 2.2 in Run 2.

Equation [2] can also be used to calculate what fraction of the reduction could have taken place by transfer of hydrogen from the α- and γ-positions of the Grignard without producing a detectable amount (0.01% by weight) of deuterium in the water of combustion from the resulting benzhydrol. If it is assumed that the isotope effect in these hypothetical reductions is six, a value near the maximum allowed by theory and experience (3), then it is found that the maximum per cent of reduction which could have escaped detection is 17% from the α-position and 1% from the γ-position. The value is large in the α-position because a short supply of lithium aluminum deuteride necessitated a low concentration of deuterium in the α-deuteroisobutyl bromide. However, it seems reasonable to suppose that the reaction takes place by one mechanism and not several, and since it is evident that the reduction does involve the β-hydrogen and that not more than 17% of it can involve α-hydrogen, it is highly probable that the reduction takes place by transfer of β-hydrogen exclusively.

[4]*That deuterium is not lost from the alkyl groups of alkyl halides or alcohols during formation or hydrolysis of metal derivatives is shown by the work of Shiner (16).*

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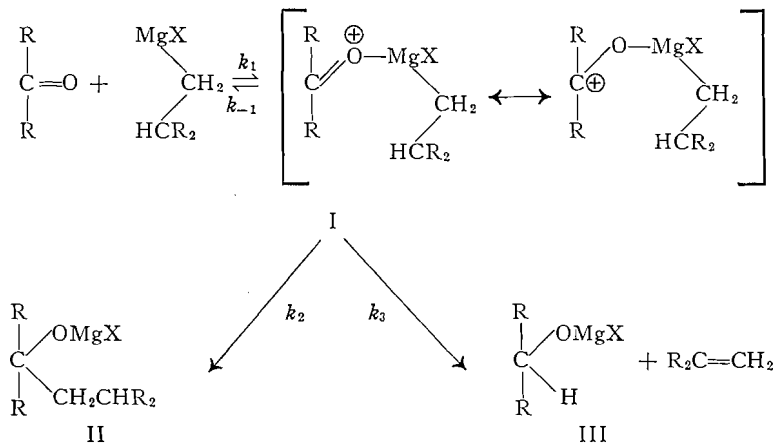
The deuterium analyses on dimethylmalonic acid and β-deuteroisobutyl alcohol can be used to calculate the isotope effect in the decarboxylation reaction

$$(CH_3)_2C(COOD) \xrightarrow[-CO_2]{\text{heat}} (CH_3)_2CDCOOD \xrightarrow{LiAlH_4} (CH_3)_2CDCH_2OH.$$

Here it is desired to compare the D/H ratio in the carboxyl groups of dimethylmalonic acid with that on the α-carbon atom of the isobutyric acid obtained from it. Since only carbon dioxide is lost during the decarboxylation itself, the over-all deuterium to protium ratio in the two compounds will be the same. Actually, isobutyric acid was analyzed and the result applied to both acids. Analysis of the isobutyl alcohol obtained from the isobutyric acid gave the D/H ratio on the β-carbon of the alcohol, which should be the same as that on the α-carbon of the isobutyric acid. Use of these ratios in Equation [2] gave a calculated isotope effect, k_H/k_D, of 4.5.

DISCUSSION

A variety of mechanisms have been suggested for the reducing action of the Grignard reagent, and these have been reviewed recently by Kharasch and Reinmuth (8). Probably the most satisfactory of these is the mechanism proposed by Whitmore, or some modification of it. Whitmore proposed (19) that the carbonyl oxygen co-ordinates with the Grignard magnesium forming a six-membered ring complex, I, which can either rearrange to addition products, II, or transfer a hydrogen from the β-carbon of the Grignard to the carbonyl carbon to give reduction products, III. This mechanism of reduction,



or something very like it, is given strong support by the asymmetric reductions accomplished by Mosher and LaCombe (12).

Our experimental results tend to support the Whitmore mechanism since they show that the reducing hydrogen does come from the β-carbon of the Grignard reagent as Whitmore (and many others) proposed. They do not, of course, support or contradict the theory that reduction takes place through hydrogen transfer within a complex. However, if it is assumed that such a complex is involved in the reaction, then our results show that the complex is

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in equilibrium with reactants, and that the rate of attainment of equilibrium is greater than the rate of decomposition of complex to reduction products. This is evident from the following considerations. The substitution of deuterium for protium on the β-carbon of the Grignard reagent should have no significant effect on the rate of co-ordination between magnesium and oxygen; hence deuterated and undeuterated complex should be formed in the ratio in which deuterated and undeuterated Grignard reagents were introduced. Then if every complex decomposed into reduction products (in our reaction there were no other products) the ratio of deuterium to protium in the labelled position of benzhydrol would be the same as that in the isobutyl bromide from which it was made. But an isotope effect of about two was observed, so that not every complex can decompose to alcoholate and olefin. That is, k_{-1} in the mechanism scheme above must be greater than k_3.

An interesting modification of the Whitmore mechanism has been proposed by Swain (17). From a consideration of the order of reactivity of a series of Grignard reagents toward nitriles and carbonyl compounds he concludes that, while reduction takes place by the decomposition of a complex as proposed by Whitmore, addition must take place by attack of a second Grignard molecule on the complex. Support for this theory was found in the observation that when magnesium bromide is added to the carbonyl solution prior to the Grignard reagent the yield of addition product is increased at the expense of reduction (18). This is explained by pointing out that magnesium bromide should be a better complexing agent than the Grignard reagent, and that a complex between carbonyl compound and magnesium bromide would be incapable of reductive hydrogen transfer but would still be subject to attack by a Grignard molecule leading to addition.[5]

McBee, Pierce, and Meyer have shown by a series of vapor pressure measurements in phenetole that magnesium bromide does complex some ordinary aldehydes and ketones, but that no complex is formed with analogous fluorinated carbonyl compounds (11). Since Grignard reagents should complex less readily than magnesium bromide, these authors conclude that reduction of fluorinated carbonyl compounds takes place without intermediate complex formation. Nevertheless, McBee, Pierce, and Higgins have shown that added magnesium bromide favors addition and hinders reduction of fluorinated aldehydes and ketones just as with non-fluorinated compounds (10). This seems to throw some doubt on the interpretation by Swain and Boyles of the mechanism of the action of added magnesium bromide.

However, it may be noted that the vapor pressure measurements on solutions of magnesium bromide and fluorinated carbonyl compounds actually show that the equilibrium concentration of complex is very low, not that no complex is formed. So long as the rate of attainment of equilibrium is fast the

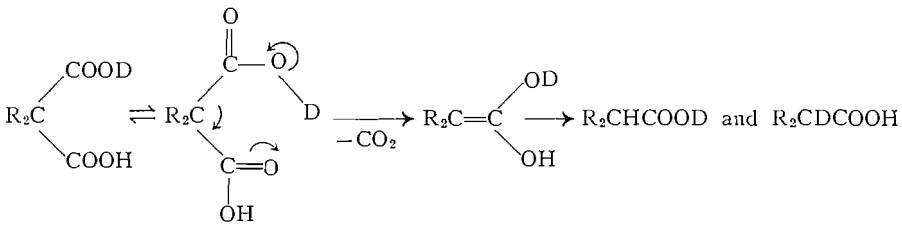
[5]*It has long been thought that magnesium halide is also in equilibrium with the Grignard reagent itself (5, 7).*

$$2RMgX \rightleftharpoons R_2Mg + MgX_2$$

If both RMgX and R_2Mg enter into reaction with carbonyl compound, and if R_2Mg is a better reducing agent (or poorer adding agent) than RMgX, then the results of Swain and Boyles can be explained simply by the effect of added magnesium bromide on this equilibrium. Some support, but certainly not proof, is given this alternative explanation by the work of Noller on the reducing action of diisobutylmagnesium on benzophenone (13).

reduction could still take place through a complex even though its concentration were never large. Thus the interpretation of the effect of added magnesium bromide could still be that of Swain and Boyles. The isotope effect observed in the present work shows that if a complex is formed it does reach equilibrium with its components rapidly, at least in the case of benzophenone and isobutylmagnesium bromide. Hence the possibility that Grignard reduction of fluorinated carbonyl compounds takes place through a complex is still open.

The isotope effect observed in the decarboxylation of dimethylmalonic acid throws little light on the mechanism of that reaction. A reasonable mechanism has been proposed by King (9) which predicts the observed isotope effect:



Indeed, the symmetry of the molecule is such that it is difficult to devise a mechanism which does not predict an isotope effect. The fact that one does exist is simply noted in passing.

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NOTES

PREPARATION OF D- AND L-GLYCERALDEHYDE FROM KETOHEXOSES*

By A. S. Perlin and Carol Brice

When D-fructose is treated in acetic acid with lead tetraacetate two moles of oxidant are consumed rapidly and the reaction then virtually ceases (6, 11). The product of this oxidation, isolated in approximately 90% yield, is a formic acid – glycolic acid diester of D-glyceraldehyde (11). Hydrolysis of the ester groups with dilute acid affords D-glyceraldehyde. L-Sorbose reacts with lead tetraacetate in the same way yielding a formate–glycolate diester of L-glyceraldehyde and finally, by hydrolysis, L-glyceraldehyde. The over-all yield from each ketose, as determined by hypoiodite titration and from the apparent chromatographic purity of the preparations, is 80 to 90% of theory. Each compound has been characterized as its dimedon derivative. Crystalline DL-glyceraldehyde is obtained in 85% yield by oxidation of an equimolar mixture of D-fructose and L-sorbose. This high degree of conversion may be contrasted with that of 16.2% over-all yield from acrolein (9) and of 17.5% from monoacetone glycerol (4).

Freshly prepared, the D- and L-isomers have specific optical rotations, respectively, of $+8.3°$ and $-8.6°$. According to Baer and Fischer (1), the specific rotation of D- and L-glyceraldehyde is $\pm 14°$ if the compound is first dried *in vacuo* at 55°C. This observation has been confirmed using the currently-described L-glyceraldehyde sample which, after the prescribed treatment, shows an initial specific rotation of $-14.3°$. The infrared absorption spectra of the D-, L-, and DL-compounds are identical. Absorptions at the carbonyl frequencies are very weak, which agrees with the known tendency of glyceraldehyde to dimerize by forming a hemiacetal linkage between the aldehyde group of one molecule and an hydroxyl group of a second molecule (16, 1). The spectrum of the crystalline DL-dimer differs slightly from that of the same compound as a sirup, and carbonyl bands are absent.

The present results show that the degradative oxidation of ketohexoses provides a facile method for preparing the relatively rare trioses directly from readily available sugars, which may be more advantageous in some instances than the procedures of Fischer and Baer (1, 3). Limited oxidation of D-glucose with periodate, reported recently by Schöpf and Wild (13), constitutes another convenient source of the D-isomer. The preparation of tetroses from aldohexoses and of trioses from aldopentoses has been described elsewhere (10) and is analogous to the present procedure. Oxidation of a pentose, however, is not quite as favorable to the formation of glyceraldehyde as is the degradation of a ketohexose since, with the former, some overoxidation occurs (11),

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the yield of triose is smaller, and traces of pentose and tetrose are also found together with the triose (10). Moreover, D-fructose and L-sorbose are among the least costly of sugars and they are therefore especially desirable as starting materials.

Oxidation of ketohexoses by the reaction described has been suggested (11) as a possible procedure for degrading D-fructose labelled with carbon-14.

EXPERIMENTAL

D-Fructose, L-sorbose, and all solvents were of reagent grade quality. Lead tetraacetate was prepared according to the procedure recommended by Vogel (14), or was obtained commercially (Matheson Co., Inc.), both samples being equally satisfactory.

Solutions were concentrated *in vacuo* at 35–40°C.

D-*Glyceraldehyde*

D-Fructose (5.0 gm., 0.028 mole) was dissolved in 8 ml. of water* and the solution was diluted with 500 ml. of glacial acetic acid. Lead tetraacetate (26.1 gm. dry weight, 0.059 mole) was added to the solution with vigorous stirring and, 20 min. after the oxidant had dissolved, the lead was precipitated by adding 50 ml. of a 10% solution of oxalic acid in acetic acid. Stirring was continued for a further 20 min. and the suspension was filtered. The filtrate was concentrated to the consistency of a thin sirup and the product was extracted into ethyl acetate, the insoluble lead salts being filtered off. Removal of the ethyl acetate afforded sirupy D-glyceraldehyde formate–glycolate diester, 4.6 gm. (94% yield). The diester (2.3 gm.) was dissolved in 75 ml. of 0.05 *N* sulphuric acid and the ester groups were hydrolyzed by heating for eight hours at 50°C. Sulphuric acid and the liberated formic and glycolic acid were removed by portionwise addition with vigorous stirring of Dowex-1 resin (200–400 mesh; regenerated with 1 *N* sodium bicarbonate). The resin was filtered off and washed well on the filter with water. Hypoiodite titration (15) indicated that the combined neutral filtrates contained 1.13 gm. of D-glyceraldehyde (89% yield based on D-fructose). The specific rotation of the D-glyceraldehyde in this solution was $[\alpha]_D^{27}$ +8.3° (*c*, 0.75).

On paper chromatograms, using ethyl acetate/pyridine/water (8) and methyl ethyl ketone/water (2) as solvents, the product moved at the same rate as L-glyceraldehyde prepared from L-arabinose (10), both compounds exhibiting some streaking. No other sugars appeared to be present, urea oxalate spray (5) being used to test for the presence of fructose. With aniline oxalate spray (7) D-glyceraldehyde gave a deep brown color and under ultraviolet light a mauve fluorescence which faded after a short period. The infrared absorption spectrum, obtained with the potassium bromide window technique (12), was identical with that of L-glyceraldehyde prepared from L-arabinose.

D-*Glyceraldehyde Dimedon*

A solution of 0.30 gm. of D-glyceraldehyde in 60 ml. of phosphate buffer

**Aqueous acetic acid has been shown to be suitable for many lead tetraacetate oxidations (E. Baer, J. M. Grosheintz, and H. O. L. Fischer, J. Am. Chem. Soc. 61: 2607. 1939).*

(containing 2 ml. of 1 *M* monopotassium phosphate and 1.2 ml. of 1 *N* sodium hydroxide) was treated with 1.1 gm. of dimedon dissolved in 10 ml. of ethanol, at 40°C. for five hours and then at room temperature for 18 hr. The crystalline product which settled out was filtered off, washed with water, and dried *in vacuo*. A second crop of crystals was obtained by concentrating the filtrate. The total weight of derivative was 0.82 gm. (73% yield); melting point, 194–200°C., undepressed by admixture with L-glyceraldehyde dimedon (10); $[\alpha]_D^{27}$ +208° (*c*, 0.6, ethanol). The infrared absorption spectrum of the derivative was identical with that of L-glyceraldehyde dimedon. Calc. for $C_{19}H_{26}O_5$: C, 68.24%, H, 7.84%; found: C, 68.26%, H, 7.81%.

L-Glyceraldehyde

L-Glyceraldehyde was prepared in 82% yield from L-sorbose by a procedure identical with that described above for preparing D-glyceraldehyde. Its specific rotation was $[\alpha]_D^{27}$ −8.6° (*c*, 3.6, water). An aliquot of the solution was concentrated, and the sirupy L-glyceraldehyde obtained was heated *in vacuo* at 55°C. for two hours and then redissolved in water; $[\alpha]_D^{27}$ −14.3° (*c*, 5.5).

The product appeared to be chromatographically pure and its infrared spectrum was identical with those of L- and DL-glyceraldehyde. It gave a 71% yield of L-glyceraldehyde dimedon; m.p., 197–198.5°C., undepressed by admixture with the derivative of the D-isomer; $[\alpha]_D^{27}$ −210° (*c*, 0.6, ethanol). Calc. for $C_{19}H_{26}O_5$: C, 68.24%, H, 7.84%; found: C, 68.27%, H, 7.78%.

DL-Glyceraldehyde

An equimolar mixture of D-fructose and L-sorbose (1.0 gm.) was oxidized under the conditions described above in the preparation of D-glyceraldehyde. The crude diester was taken up directly in 0.05 *N* sulphuric acid for hydrolysis of the ester groups, without previous extraction into ethyl acetate. The slightly turbid hydrolyzate was neutralized with the Dowex-1 resin and concentrated, yielding a clear, colorless sirup which was dried *in vacuo* over phosphorus pentoxide; weight 0.48 gm.; $[\alpha]_D^{27}$ 0°±0.1° (*c*, 3, water). Sirupy DL-glyceraldehyde (42 mgm.), spread as a thin film on a microscope slide, solidified completely in two weeks at room temperature; weight, 38.5 mgm. (87% yield from starting material), melting point, 117–122°C. A mixed melting point with authentic DL-glyceraldehyde* (m.p. 145–147°C.) was 122–132°C. The infrared absorption spectrum and the X-ray diffraction pattern of the crystalline compound were identical with those of authentic crystalline DL-glyceraldehyde. Calc. for $C_3H_6O_3$: C, 40.0%, H, 6.71%; found: C, 39.58%, H, 6.65%. The compound contained 1% ash. A purer specimen was obtained by extracting DL-glyceraldehyde sirup with acetone, the acetone extract depositing crystals which melted at 138–140°C., undepressed by admixture with authentic DL-glyceraldehyde.

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**Delta Chemical Works, New York 23, N.Y.*

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ON THE MEASUREMENT OF CHARGE ON INDIVIDUAL FIBERS

BY C. E. MOSSMAN* AND SIR ERIC RIDEAL

METHOD

The purpose of the experiments described here was to obtain a measure of the charge on a single fiber, by observing the deflection of such a fiber suspended in aqueous solution and under the action of an applied electric field. The effect of varying the field strength and the concentration of the different solutions was also investigated.

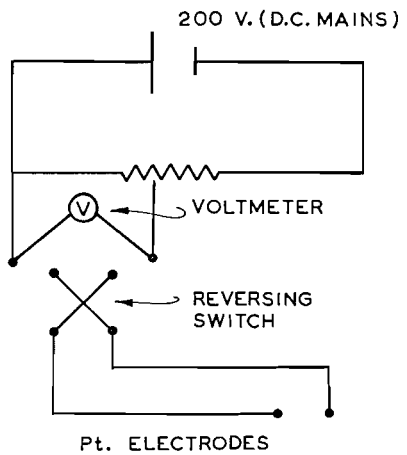

FIG. 1. Electric circuit.

The electric circuit used is shown in Fig. 1. The applied voltage could be varied from 0 to 200 v. (d-c.).

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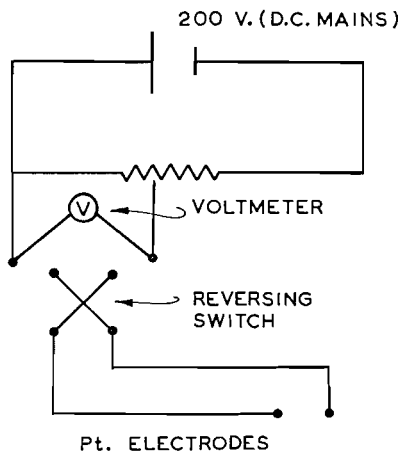

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It was originally attempted to suspend the fiber (in this case, glass) by bending one end into the form of a hook or loop. The fiber was then suspended at right angles from a fine glass hook between the platinum electrodes. Difficulty was encoutered because of friction at the point of contact of the hooks, which prevented the fiber from swinging freely. Deflections were measured by means of a travelling microscope.

A more satisfactory method of carrying out the measurements involved setting up a torsion balance. A fine quartz suspension was used as the torsion fiber. This was attached at the top to the torsion head with wax, and was held vertically by the weight of a quartz bead (W) glued to the bottom, as shown in Fig. 2. The fiber to be investigated (F), which was approximately 3 cm. in

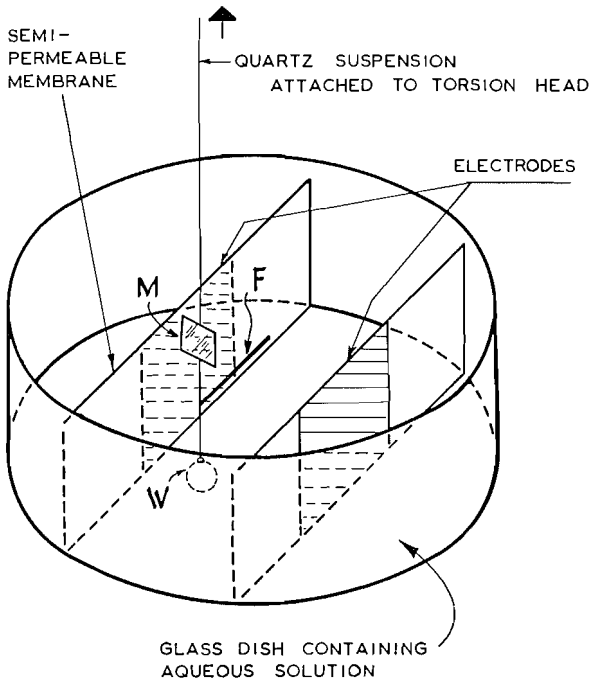

FIG. 2. Method of suspending the fiber between the electrodes.

length, was fastened at right angles to the quartz suspension. The whole system was arranged so that this fiber would be in the solution midway between the electrodes, which were of platinum foil. A small mirror (M) was attached to the quartz suspension just above the fiber, and a light beam was reflected from this mirror on to a circular scale. When the electrical field was applied, the degree of deflection could be measured by the twist of the calibrated quartz suspension, as indicated by the moving light beam.

It was immediately apparent that steady deflections could only be obtained in dilute solution, because of bubble formation and convection currents which interfered with the motion of the fiber when concentrated solutions were used.

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The effect of convection currents was greatly reduced by separating each electrode from the fiber by a strip of semipermeable membrane, e.g., porous rubber. A flat electrophoresis cell was approximated by placing the fiber between two horizontally parallel glass slides (not shown in diagram). This also seemed to decrease the heating effect.

The quartz fiber was suspended inside a glass tube to eliminate any possible error due to draughts, and the whole system was placed on a wall mount to minimize vibration effects, to which it was extremely sensitive.

In order to use this torsion method, it is essential that the fiber whose deflection is to be measured be rigid. Glass and quartz were the fibers employed in the earlier exploratory runs; later terylene fiber was used.

The terylene fibers were cleaned by being placed in the thimble of a Soxhlet extractor, where they were washed with a propanol–water solution (60:40 by volume) for one hour. They were then stored in propanol until used. The fibers were always handled with tweezers in order to reduce risk of contamination.

The torsion constant (dynes/radian) for each quartz suspension used was determined by measuring the period of oscillation with and without a small body of known moment of inertia being attached to the quartz weight.

RESULTS

The results of these measurements were generally plotted as deflection (in centimeters of the circular scale, which was also calibrated in radians/cm.) against applied voltage. The actual potential gradient was not used (v./cm.). Since the electrode separation was always approximately 3.0 cm., it was felt that no great error was introduced by comparing results for different fibers at a given applied voltage.

An example of these plots for terylene in distilled water is given in Fig. 3, and shows that the deflections were reproducible in the opposite direction when

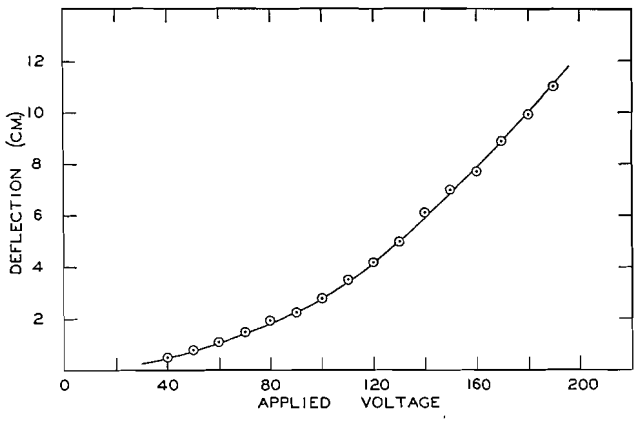

FIG. 3. Fiber deflection vs. applied voltage for terylene in distilled water. • Deflections to right: ○ deflections to left. Fiber length = 3.5 cm.; τ = 0.212 dyne/radian; scale calibration = 1.94×10^{-2} radian/cm.

the direction of the current was reversed. Consecutive measurements on a given fiber were also reproducible. As might be expected, the deflection for a given applied voltage increased with increasing fiber length. The relation between deflection and applied voltage appeared to be nonlinear.

All the fibers were found to possess a negative charge in distilled water and dilute HCl solutions. This charge was reversed when dilute $Th(NO_3)_4$ was the electrolyte.

Some measurements were also carried out using solutions of such detergents as sodium octadecyl sulphate and sodium dodecyl sulphate. Although a small concentration of sodium octadecyl sulphate ($\sim 2 \times 10^{-6}$ molar) seemed to increase slightly the negative charge on the fiber over that observed in distilled water, further addition of the solution had no appreciable effect.

Results of a representative run using varying concentrations of sodium dodecyl sulphate are plotted in Fig. 4. In each case an initial increase in the negative charge was observed, followed by a continuous decrease with increasing detergent concentration.

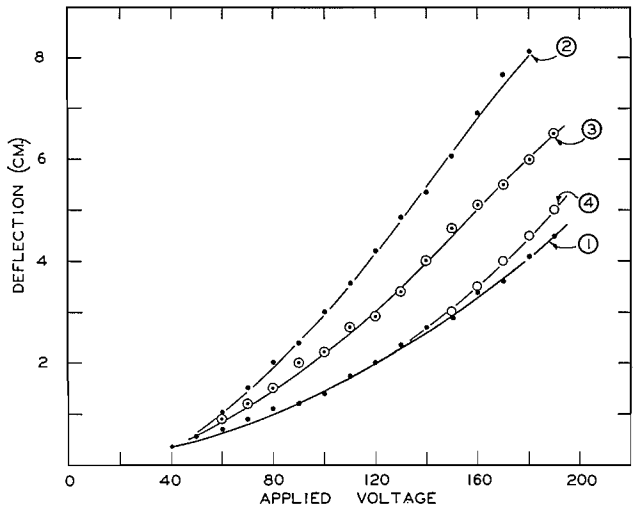

FIG. 4. Fiber deflection vs. applied voltage for terylene in (1) distilled water; (2) 4×10^{-5} M sodium dodecyl sulphate; (3) 8×10^{-5} M sodium dodecyl sulphate; (4) 2×10^{-4} M sodium dodecyl sulphate. Fiber length = 3.05 cm.; $\tau = 0.180$ dyne/radian; scale = 1.94×10^{-2} radian/cm.

Exploratory measurements were also made using solutions of orange II dye. Results of one run are shown in Fig. 5.

It had been hoped to investigate any variation in the charge on nylon fibers having different equivalent numbers of COOH and NH_2 groups. However the fiber samples obtained were not rigid, so that no convenient means of carrying out the measurements with the present system could be found.

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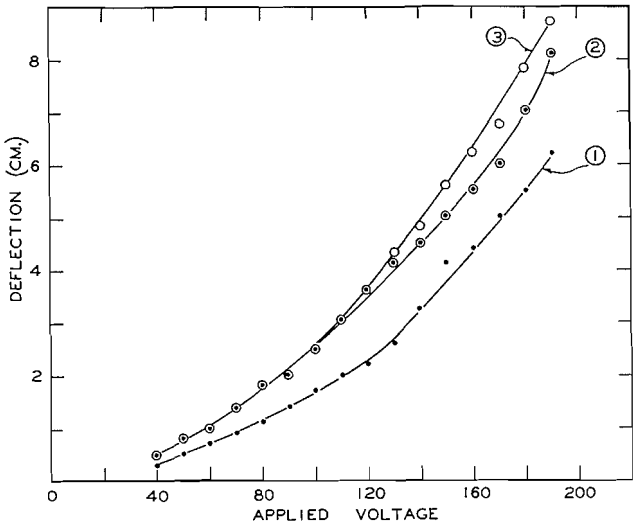

FIG. 5. Fiber deflection vs. applied voltage for terylene in: (1) distilled water; (2) 4×10^{-5} M dye; (3) 8×10^{-5} M dye. Fiber length = 3.2 cm.; τ = 0.19 dyne/radian; scale = 1.94×10^{-2} radian/cm.

DISCUSSION

The effect is recognized as an electrokinetic effect, comparable to electrophoresis.

However, since the equilibrium point of the deflection rather than the *rate* of deflection has been determined, it must be expected that this would represent a measure of the charge on the fiber rather than of the zeta-potential. The charge, q (e.s.u./cm.^{2}), would then be related to the fiber potential, ψ, which is not necessarily identical with the zeta-potential, by the equation:

$$q = \sqrt{\frac{2DnkT}{\pi}} \sinh\left(\frac{ze\psi}{2kT}\right).$$

Although the method appears to give a qualitative measure of the fiber charge, several difficulties are evident when an attempt is made to interpret the results quantitatively.

Considering first a spherical particle fastened to the end of an uncharged rod, the moving force on this particle would be:

$$F = E.q,$$

where E is the applied potential gradient and q the charge on the particle. The restoring force may be expected to be equal to $\tau\theta/h$, where h is the distance from the sphere to the torsion wire, τ is the torsion constant, and θ is the deflection of the fiber from an initial position parallel to the electrodes.

However, in the case of a charged cylindrical fiber, it is difficult to know what the moving force will be. The force per unit of fiber surface may again be $E.q$, but the correct expression for the total force would have to take into

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account the fiber length. It would also be probable that the force on the part of the fiber nearest the torsion wire would be less than the force acting on the end of the fiber, which would be closer to the electrode.

Taking the force per unit of surface as $E.q.\cos\theta$, it should be equal and opposite to the restoring force, $\tau\theta/h$, where h in this case is the length of the fiber. Then

$$E = \frac{\tau}{hq}\frac{\theta}{\cos\theta}$$

and $\theta/\cos\theta$, rather than θ, should be plotted against E. In actual practice, however, θ is so small that $\cos\theta$ is very close to unity over the whole range of potentials; the plots are therefore no more linear than those shown in Figs. 3 to 5.

Thus, while the method outlined here gives promise of being useful for the determination of relative charge densities, no absolute values can be calculated from the measurements already made until more is known of the nature of the forces acting on the fiber. In any further work along this line, it is recommended that a means of temperature control for the system be introduced.

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THE SYNTHESES OF SUGARS FROM SMALLER FRAGMENTS

PART X. SYNTHESIS OF L-GLUCOHEPTULOSE[1]

BY J. K. N. JONES[2] AND R. B. KELLY[3]

ABSTRACT

L-*Gluco*heptulose has been prepared by the action of muscle aldolase on a mixture of L-erythrose and hexose diphosphate.

INTRODUCTION

In a previous communication (1) it was shown that propionaldehyde and hexose diphosphate together with a crude pea aldolase extract yielded 5,6-didesoxy-D-fructose. We now show that L-erythrose and hexose diphosphate with crystalline muscle aldolase yield L-*gluco*heptulose phosphate from which the free sugar was prepared. It had been demonstrated previously (2) that if L-erythrose is replaced by its optical isomer, D-sedoheptulose phosphate resulted. We have confirmed this observation. These are further examples of the rule that aldolase of plant or animal origins will transfer dihydroxyacetone phosphate from hexose diphosphate to an aldehyde with the formation of a derivative of D-*threo*pentulose.

In experiments with crude pea aldolase preparations it was observed that L-erythrose condensed with hexose diphosphate with the formation of small amounts of a heptulose sugar which was identified chromatographically (cf. 4) as *gluco*-heptulose. Further work with a purer enzyme preparation will be required before this sugar can be positively identified.

EXPERIMENTAL

Crude pea aldolase was prepared according to the method of Hough and Jones (3). The crystalline muscle aldolase was supplied by Nutritional Biochemical Corporation.

Erythrose and threose were prepared by Ruff degradation (6) of the corresponding calcium arabonates and xylonates according to the method of Overend, Stacey, and Wiggins (5).

IR 120 resin and IR 4B resins were purified before use. The former was treated with ammonia, washed with water, and then treated with 2 *N* hydrochloric acid and again washed with water until the washings were neutral.

[1]*Manuscript received October 18, 1955.*
Contribution from the Department of Chemistry, Queen's University, Kingston, Ontario.
[2]*Department of Chemistry, Queen's University, Kingston, Ontario.*
[3]*Merck & Company Limited, Montreal, Quebec.*

The latter was treated with 2 *N* sodium hydroxide, washed with water, and then converted to the acetate form before use by reaction with 8 *N* acetic acid.

Preparation of L-*Glucoheptulose*

A solution of the sodium salt of hexose diphosphate (5.0 gm.) and L-erythrose (2.5 gm.) in water (80 ml.) was adjusted by addition of acetic acid to a pH of 6.8. Dialyzed muscle aldolase (100 mgm.) in water (20 ml.) was added and the solution incubated first at room temperature for four hours and then at 37°C. for 14 hr. Sulphuric acid (100 ml., 2 *N*) was then added and the solution heated briefly at 80°C. to coagulate protein. After filtration the solution was boiled for three and a half hours, cooled, and neutralized with barium carbonate. Precipitated inorganic material was removed by filtration and the filtrate deionized on IR 120 and IR 4B acetate resins. Concentration of the resultant neutral solution gave a resin (1.7 gm.) which contained a heptulose sugar contaminated with traces of fructose (paper chromatography). After treatment with charcoal, the sirup crystallized from alcohol to yield L-*gluco*-heptulose (400 mgm.) with m.p. 171–173°C. (not depressed on admixture with an authentic sample) and $[\alpha]_D$ −65° (*c*, 1.0 in water). The powdered crystals gave an X-ray diffraction pattern identical with that of an authentic specimen, kindly supplied by Dr. N. K. Richtmyer.

Preparation of Sedoheptulosan

The sodium salt of hexose diphosphate (6.0 gm.) in water (50 ml.) was added to a solution of D-erythrose (3.2 gm.) in water (30 ml.). The resulting solution was adjusted by addition of acetic acid to a pH of 6.8. A dialyzed solution of muscle aldolase (100 mgm.) in water (20 ml.) was added and the solution incubated at 25°C. for four hours and then at 37°C. for 14 hr. The solution was then heated briefly to 80°C. to coagulate protein and filtered. Sulphuric acid (100 ml. 2 *N*) was added and the solution boiled for three hours. The cooled solution was then made alkaline by addition of barium hydroxide, solids were removed by filtration, and the filtrate was boiled for two and a half hours. The cooled solution was neutralized with dilute sulphuric acid, filtered, and the filtrate concentrated. The concentrate was deionized on IR 120 and IR 4B resins and the neutral solution decolorized with charcoal. Concentration of the filtrate gave a sirup which crystallized from 95% alcohol furnishing sedoheptulosan hydrate (520 mgm.). Recrystallization from methanol gave the pure sugar, m.p. 93°C. with $[\alpha]_D$ −130° (*c*, 18.5 in water). The material did not depress the melting point of an authentic sample, kindly supplied by Dr. N. K. Richtmyer; the two samples were indistinguishable on paper chromatograms. The powdered crystals gave an X-ray diffraction pattern identical with that of an authentic specimen.

Incubation of L-*Erythrose with Hexose Diphosphate*

A solution of L-erythrose (4.0 gm.) in water (25 ml.) was added to a solution of hexose diphosphate (sodium salt, 8 gm.) in water (40 ml.), the pH of the solution was adjusted to 6.8 by the addition of acetic acid, and to this solution was added a solution of pea aldolase (100 ml. from 100 gm. seed). The solution

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was incubated at 37°C. for 14 hr. The pH was then adjusted to 5 (acetic acid) and the solution was heated briefly at 80°C. to coagulate protein. The precipitate was removed on the centrifuge and the supernatant solution was then passed down a column of IR 120 resin. The acidic solution was concentrated to 50 ml. and then boiled for two hours. The cooled solution was passed down a column of IR 4B resin and the neutral effluent concentrated to a sirup (1.12 gm.). The sirup contained heptulose which was separated on a column of cellulose using butan-2-ol–water (10:1) as solvent. The heptulose fraction was contaminated with fructose. Further purification was effected by chromatography on sheets of Whatman No. 1 paper using ethyl acetate – acetic acid – formic acid – water (4:3:1:4) as solvent. Elution of the appropriate section of the paper gave a sirupy heptulose (100 mgm.) which failed to crystallize. It yielded an osazone, m.p. 202–203°C. (sintering at 197°C.) with $[\alpha]_D$ −35° (*c*, 5.6 in pyridine alcohol 2:3). Anal.: Calc. for $C_{14}H_{24}N_4O_5$: C, 60.3; H, 6.2. Found: C, 59.9, H, 6.1. The osazone of D-*gluco*heptulose has m.p. 194–196°C. (sintering at 187°C.) with $[\alpha]_D$ +36°; that of D-*manno*heptulose has m.p. 193–196°C. (sintering at 190°) with $[\alpha]_D$ +36° (solvent as above).

Unfortunately well-defined X-ray diffraction patterns of the osazones could not be obtained. The rate of movement of the sugar was close to that of *gluco*heptulose and *manno*heptulose in several solvent systems. It could be differentiated from all other heptuloses except *allo*heptulose, no specimen of which was available.

The authors thank the National Research Council for financial assistance and for the award of a Postdoctorate Fellowship to one of them (R. B. K.). They also thank Dr. N. K. Richtmyer for the generous gift of heptulose samples.

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ORGANIC DEUTERIUM COMPOUNDS

XIV. PREPARATION OF DEUTERATED METHYL BENZENES[1]

By R. Renaud and L. C. Leitch

ABSTRACT

The synthesis of toluene-α-d_3, *o*-chlorotoluene-α-d_3, and *m*-xylene-α,α'-d_6 from benzotrichloride, *o*-chlorobenzotrichloride, and α,α' hexachloro-*m*-xylene respectively is reported using zinc and acetic acid-*d* as the dechlorinating agent. The preparation of acetic acid-*d* of optimum isotopic purity is described.

The reduction of alkyl halides with zinc and acetic acid-*d* has been recommended by Schissler, Thompson, and Turkevich (4) for the preparation of deuterated methanes, ethanes, and propanes in preference to the hydrolysis of Grignard reagents with deuterium oxide, or else dehalogenation of halides with lithium aluminum deuteride or zinc and methanol-*d*. Their method has now been extended successfully to the preparation of methyl benzenes deuterated in the side chain.

According to the literature (1) benzotrichloride reacts with zinc, alone or in the presence of ether, to give tolane dichloride; toluene has never been reported to be a product of this reaction. Preliminary experiments using zinc dust and acetic acid in ether also gave predominantly tolane dichloride but traces of toluene as well. As a result of several experiments in which the effect of temperature, order of adding the reagents, and ratio of acid to halide were studied, a procedure was developed which consistently gave 70 to 80% yields of toluene. It consists in adding benzotrichloride slowly to a stirred suspension of zinc dust and acetic acid in absolute ether while keeping the temperature of the reaction mixture below +4°C. Under these conditions little if any tolane dichloride is formed. These experiments indicated that this reaction would be satisfactory for the preparation of deuteromethyl benzenes.

TABLE I

Source of acetic acid-*d*	Deuterium content of toluene-α-d_3			
	Mol. % $C_6H_5CD_3$	Mol. % $C_6H_5CHD_2$	Mol. % $C_6H_5CH_2D$	At. % D
1. Acetic anhydride	66.1	29.2	4.7	87.0
2. Freshly distilled acetic anhydride	79.7	18.7	1.6	92.6
3. Acetic anhydride distilled over Mg	82.9	15.8	1.3	93.3
4. Acetyl chloride redistilled	89.5	10.5	—	96.5
5. Acetyl chloride distilled over $C_6H_5NMe_2$	95.6	4.1	0.3	98.5
6. Silver acetate+DBr	39.3	41.5	16.5	70.5

The preparation of toluene-α-d_3 therefore depended upon obtaining acetic acid-*d* of high isotopic purity. With acetic acid-*d* prepared by the hydrolysis of

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freshly distilled acetic anhydride with deuterium oxide (99.6%) the deuterium content of the toluene was unexpectedly low as shown in the figures for experiment 2 in Table I. A slight improvement was evident using acetic anhydride that had been refluxed with magnesium turnings for two days before distillation. Acetic acid-*d* prepared by hydrolyzing redistilled acetyl chloride gave still better results. Toluene-α-d_3 of optimum purity was obtained from acetic acid-*d* which had been prepared by distilling acetyl chloride over dimethylaniline and hydrolyzing it with deuterium oxide. The dimethylaniline evidently combines with traces of dissolved hydrogen chloride in the acetyl chloride. With trifluoroacetic acid-*d* the yields of toluene were very poor and the isotopic purity was low. Acetic acid-*d* prepared by decomposing anhydrous silver acetate with deuterium bromide likewise gave a product of low deuterium content.

The same reaction was used to prepare *o*-chlorotoluene and *m*-xylene deuterated in the methyl groups and can probably be extended to the preparation of other related compounds if the required chloro derivatives are available. In this connection *o*-xylene deuterated in the methyl groups could probably not be prepared with a high deuterium content because in the chlorination of *o*-xylene by the method of Miller (5) the maximum number of chlorine atoms that can be introduced in the side chains is five, further substitution occurring in the ring.

In view of the high *m*-orienting capacity of the trichloromethyl group it is possible that the procedure just described may afford a new route to *m*-substituted derivatives of toluene which are at present accessible with difficulty. This aspect of the work is currently under investigation.

With respect to the mechanism of the reaction the formation of tolane dichloride would at first lead one to believe it is homolytic:

$$C_6H_5CCl_3 + Zn \rightarrow C_6H_5\dot{C}Cl_2 + ZnCl$$

$$2C_6H_5\dot{C}Cl_2 \rightarrow C_6H_5CCl_2CCl_2C_6H_5$$

$$C_6H_5CCl_2CCl_2C_6H_5 \xrightarrow{Zn} C_6H_5CCl{=}CClC_6H_5.$$

Toluene would be formed by attack of the dichlorobenzyl radical on acetic acid:

$$C_6H_5\dot{C}Cl_2 + CH_3COOH \rightarrow C_6H_5CHCl_2 + CH_3CO\dot{O}$$

$$CH_3CO\dot{O} + ZnCl \rightarrow ZnCl(OOCCH_3).$$

However, Kharasch has established that succinic acid is the chief product of the decomposition of acyl peroxides in acetic acid (2), i.e. the free radical initially formed by decomposition of the peroxide abstracts hydrogen from the methyl group of the acetic acid to give a new free radical, $\dot{C}H_2COOH$, which dimerizes to succinic acid. Consequently benzotrichloride and acetic acid-*d* should give ordinary toluene and succinic acid if the homolytic mechanism is correct. That is apparently not the case.

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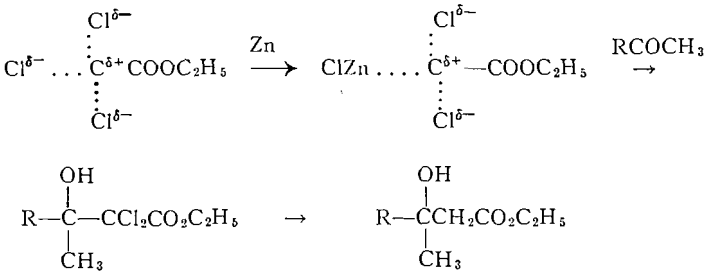
An alternative mechanism, which proceeds via an organometallic intermediate, may be written thus:

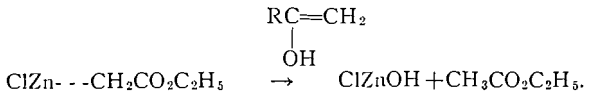
$$C_6H_5CCl_3 + Zn \rightarrow C_6H_5CCl_2ZnCl$$

$$C_6H_5CCl_2ZnCl + CH_3COOD \rightarrow C_6H_5CCl_2D + ZnCl(OOCCH_3).$$

It would be related to the mechanism proposed by Miller and Nord (3) for the Reformatsky reaction:



Ethyl acetate is formed as a by-product in Reformatsky syntheses by reaction of the enol form of the ketone with the organometallic complex:



EXPERIMENTAL

Toluene

In a 500 ml. four-necked round-bottomed flask equipped with a reflux condenser, a thermometer, a separatory funnel, and a stirrer with a thick glass blade (Tru-bor) were placed 200 ml. of anhydrous ether, 45 ml. of glacial acetic acid, and 30 gm. of zinc dust. While the stirred suspension of the zinc in the ether was kept at +3°C. by immersion of the flask in a bath of ice water, benzotrichloride (19.6 gm., 0.1 mole) dissolved in 100 ml. of ether was added over a period of four hours; stirring was continued for three hours longer. Water (200 ml.) was then added and the mixture was filtered through a wad of glass wool in a filter funnel. The ether layer was washed three times with 100-ml. portions of water, once with 10% aqueous sodium bicarbonate, and finally with water again. The ether solution was then dried over calcium chloride and distilled. The residue was distilled through a U-tube containing pellets of potassium hydroxide on the vacuum line. The distillate was fractionated through a Stedman column (12 in. $\times \frac{3}{8}$ in.). The main fraction, b.p. 110°C., n_D^{20} 1.4962, amounted to 7.8 ml. (78% of the theoretical amount). For pure toluene n_D^{20} is 1.49624.

Acetic Acid-d

(*a*) *From* $(CH_3CO)_2$ *and* D_2O

The preparation was carried out on a vacuum manifold. A mixture of 35 gm. of acetic anhydride, 1.0 gm. of zinc dust, 1 ml. of carbon tetrachloride, and a

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trace of phosphorus pentoxide in a round-bottomed flask attached through a reflux condenser to a Stock trap to the vacuum manifold was stirred for three hours. Any water or acetic acid present reacts with the zinc and halide to give methane. Deuterium oxide (7.4 ml., 99.6%) was then added to the anhydride and the mixture was stirred at 60°C. for two hours, then overnight at room temperature. The acetic acid-*d* was distilled into the Stock trap, which was cooled to −50°C. by dry ice and acetone, while the manifold was continuously evacuated. Yield: 97.2%.

(*b*) *From CH_3COCl and D_2O*

Acetyl chloride (60 ml.), redistilled over 10 ml. of dimethylaniline to remove dissolved hydrogen chloride, was treated with 5 ml. of dimethylaniline in a round-bottomed flask attached to a vacuum manifold. The solution was stirred for two hours. The acetyl chloride was then distilled into a round-bottomed flask under a cold finger condenser attached to the line through a Stock trap by placing dry ice into the finger after the line was evacuated. Deuterium oxide (14.7 ml., 99.6%) was added slowly from a funnel to the acetyl chloride while the mixture was stirred with a bar magnet. The deuterium chloride evolved was allowed to escape but if desired it could be condensed on the manifold in a trap cooled by liquid nitrogen. The reaction mixture was stirred for two hours after the deuterium oxide was added. When the line was continuously evacuated while the Stock trap was cooled in dry ice and acetone to −50°C., the acetic acid-*d* distilled over practically free of dissolved deuterium chloride. The yield was nearly theoretical.

Toluene-α-d_3

Deuterated toluene was prepared from each sample of acetic acid-*d* as described in the preparation of the normal hydrocarbon using dry equipment and ether dried over sodium. The deuterium content of each sample of toluene is shown in Table I. The best sample of toluene-α-d_3 was prepared from acetic acid-*d* obtained by hydrolysis of the chloride. For this material, n_D^{20} is 1.4953.

o-Chlorotoluene-α-d_3

This compound was prepared from *o*-chlorobenzotrichloride exactly as described for the preparation of the parent compound.

α,α′-Hexachloro-m-xylene

This compound was prepared as described by Miller (5) by the chlorination of *m*-xylene exposed in a quartz tube to ultraviolet light.

m-Xylene-α,α′-d_6

The hexachloro-*m*-xylene (31.3 gm.) was dechlorinated as described for benzotrichloride using 65.7 gm. of acetic acid-*d* prepared by the hydrolysis of acetyl chloride with deuterium oxide and 55 gm. of zinc dust. The yield of product, n_D^{20} 1.4934, was 63%. The mass analysis indicated 94 mol. % $C_6H_4(CD_3)_2$.

ACKNOWLEDGMENTS

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THE REACTIONS OF TRIFLUOROMETHYL RADICALS WITH PROPANE, *n*-BUTANE, AND ISOBUTANE[1]

By P. B. Ayscough[2] and E. W. R. Steacie

ABSTRACT

A study of the reactions of trifluoromethyl radicals, produced by the photolysis of hexafluoroacetone, with propane, *n*-butane, and isobutane has been made. The rate constants of the hydrogen-abstraction reactions have been determined at temperatures between 27°C. and 119°C. and the activation energies found to be 6.5±0.5, 5.1±0.3, and 4.7±0.3 kcal./mole respectively. These values are compared with those obtained for the reactions with methane and ethane, and with the corresponding reactions of methyl radicals.

INTRODUCTION

Hexafluoroacetone has been shown to yield trifluoromethyl radicals and carbon monoxide when irradiated with ultraviolet light in the temperature range 25° to 300°C. The reactions of these radicals with methane and ethane have already been described (3), and the rate constant for their dimerization has been determined (1). This paper describes a further extension of this work in which more complex hydrocarbons were used. It is now possible to make a more detailed comparison of the rates of abstraction of hydrogen atoms from hydrocarbons by trifluoromethyl radicals with the rates of the corresponding reactions of alkyl radicals.

EXPERIMENTAL

The apparatus was described in the earlier paper (3) and the only significant modification was the illumination of the whole volume of the cell since the lower temperatures used eliminated any possibility of reaction of the radicals with the walls of the vessel. In order to achieve a higher radical concentration some of the experiments on propane and all of those with the butanes were made using the total illumination from the B.T.H. high-pressure mercury lamp. The same sample of hexafluoroacetone was used as before, and the hydrocarbons were again Phillips research grade, distilled before use in the vacuum system and degassed in the usual way. The analytical procedure was essentially the same, except that in this work the carbon monoxide and the fluorocarbons were separated completely from the hydrocarbons by distillation in Ward stills. Mass-spectrometric and infrared spectrophotometric analysis was used to determine the hexafluoroethane/fluoroform ratios (2).

RESULTS AND DISCUSSION

Fluoroform is a major product when hexafluoroacetone is photolyzed in the presence of hydrocarbons, and in the case of reactions with propane and butane the hydrogen-abstraction is so rapid that even at room temperature the fluoro-

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form/hexafluoroethane ratio is undesirably high. The accuracy of the analyses is therefore reduced and the usable temperature range restricted, even at high radical concentrations which favor the formation of hexafluoroethane.

The proposed reaction scheme is as follows:

$$CF_3COCF_3 + h\nu \rightarrow 2CF_3 + CO \quad [1]$$

$$2CF_3 \rightarrow C_2F_6 \quad [2]$$

$$CF_3 + RH \rightarrow CF_3H + R \quad [3]$$

$$CF_3 + R \rightarrow CF_3R \quad [4]$$

$$2R \rightarrow R_2 \quad [5]$$

where RH is propane, *n*-butane, or isobutane. The products were not examined for compounds of the type CF_3R because these were present in a very small amount compared with the residual hexafluoroacetone and could not have been identified with any assurance. Some hexane was identified however when propane was the substrate, and since ethane and 1,1,1-trifluoroethane had

TABLE I

REACTIONS OF CF_3 WITH HYDROCARBONS

Temp. (°K.)	Press. CF_3COCF_3 (mm.)	Press. RH (mm.)	Time (sec.)	Products (moles/sec. $\times 10^{10}$)		$k_3/k_2^{\frac{1}{2}} \times 10^{12}$ (molecules$^{-\frac{1}{2}}$cc.$^{\frac{1}{2}}$sec.$^{-\frac{1}{2}}$)
				C_2F_6	CF_3H	
RH = propane						
300	51.7	25.2	8400	0.116	1.31	2.68
312	50.4	23.7	9000	0.217	1.92	3.32
324.5	26.2	29.7	7200	0.130	2.86	5.10
328	49.7	25.8	9000	0.149	2.62	5.04
340	28.3	20.2	7800	0.406	5.15	7.90
359	51.0	14.0	3840	3.72	21.0	16.3
372.5	38.7	20.5	3000	1.57	20.8	17.7
372.5	25.8	24.6	3600	0.74	17.8	18.2
392	30.2	15.7	3300	1.92	38.2	40.0
RH = n-butane						
302	50.1	22.9	2400	2.20	16.2	8.35
306	50.4	17.6	2400	2.37	15.6	10.3
314.5	47.5	21.0	2400	1.45	15.1	10.95
327	45.6	21.2	1800	3.90	30.6	13.95
337.5	52.7	17.3	1800	4.62	37.6	19.9
348	51.7	21.3	1800	5.31	54.1	22.4
356	51.3	18.6	1500	8.00	71.4	28.2
365.5	51.0	17.8	1200	8.87	83.1	33.4
RH = isobutane						
301	50.7	20.1	2400	0.450	11.2	15.6
302.5	51.5	18.3	2400	0.482	11.96	16.5
313	49.3	17.4	1200	0.587	16.3	22.3
318.5	50.5	12.4	1860	1.39	20.7	26.3
329	52.0	15.8	2400	1.69	39.9	30.2
338	50.0	17.5	1800	0.846	30.9	37.9
349	51.8	17.6	1110	1.88	52.7	44.4
357	51.3	12.8	1590	8.36	97.0	54.5

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been detected in the earlier experiments with methane, and butane in the products of experiments with ethane as substrate it seems reasonable to assume the same general mechanism for all these hydrocarbons. The rate constants derived for the reactions [3] would not in any case be affected by the fate of the alkyl radicals unless there was built up an appreciable concentration of some other product which produced fluoroform at a rate comparable with reaction [3]. We have therefore calculated the rate constants from the following relation, derived in the usual way:

$$k_3/k_2^{\frac{1}{2}} = \text{rate } CF_3H/[(\text{rate } C_2F_6)^{\frac{1}{2}} (RH)].$$

The reaction volume was assumed to be the cell volume (190 ml.). The results are presented in Table I, and Arrhenius plots are shown in Fig. 1. The activation energy for the reaction of trifluoromethyl radicals with propane was found to be 6.5±0.5 kcal./mole, for reaction with *n*-butane 5.1±0.3 kcal./mole, and for reaction with isobutane 4.7±0.3 kcal./mole, all about 2–3 kcal. less than

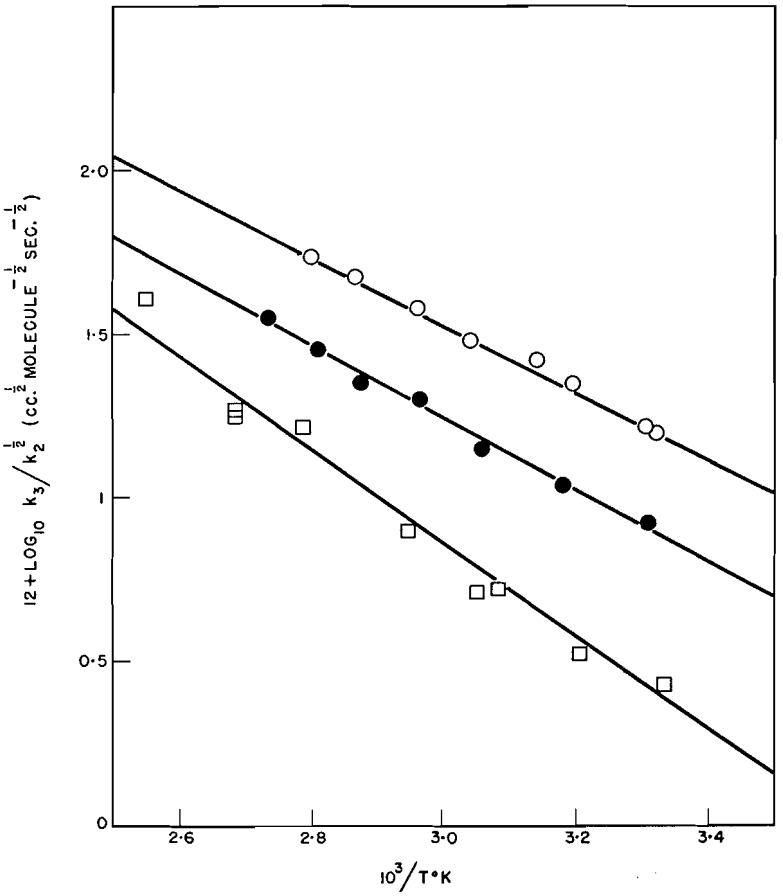

FIG. 1. Arrhenius plots of data.

the corresponding reactions of methyl radicals. This difference was noted in the case of reactions with methane and ethane (3), and in view of the work on the dimerization of trifluoromethyl radicals (1) it is certain that this difference is real and is not the result of a difference in activation energies for the radical recombination reactions.

In Table II the reactions of methyl and of trifluoromethyl radicals with hydrocarbons are compared. The steric factors have been calculated assuming

TABLE II

RATE OF HYDROGEN-ABSTRACTION FROM HYDROCARBONS

Reaction	Rate constants $k_3/k_2^{\frac{1}{2}}\times10^{13}$* (400°K.) (cc.$^{\frac{1}{2}}$ molecule$^{-\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$)	Steric factors $P_3/P_2^{\frac{1}{2}}$ (400°K.)	Activation energy (kcal./mole)	Rate constant $k_3\times10^{18}$ (400°K.) (cc. molecule^{-1} sec.$^{-1}$)	Ref.
CH_3+CH_4	0.029	14		0.017	5, 9
$+C_2H_6$	0.83	6×10^{-4}	11.4	0.49	9, 10
$+C_3H_8$	—	4×10^{-3}	9.9	—	4
$+n$-C_4H_{10}	5.8	3×10^{-4}	8.3	3.42	9, 10
+iso-C_4H_{10}	12.6	3×10^{-4}	7.6	7.43	7, 9, 10
CF_3+CH_4	3.5	6×10^{-3}	10.3±0.5	2.19	3
			9.5±2		6
$+C_2H_6$	104	6×10^{-3}	7.5±0.5	65	3
$+C_3H_8$	418	6×10^{-3}	6.5±0.5	261	This paper
$+n$-C_4H_{10}	631	2×10^{-3}	5.1±0.3	395	This paper
			5.5±1		6
+iso-C_4H_{10}	1010	2×10^{-3}	4.7±0.3	631	This paper

k_3 refers to the abstraction reaction, k_2 to the radical recombination reaction in each case.

the following collision diameters: CH_3, 3.5 Å; CF_3, 4.0 Å; CH_4, 3.5 Å; C_2H_6, 4.5 Å; C_3H_8, 5.2 Å; n-C_4H_{10}, 5.9 Å; iso-C_4H_{10}, 5.8 Å. The activation energies given assume zero activation energy for the radical recombination reactions. In order to calculate the absolute rate constants, $k_{400°K.}$, we have used the values 3.5×10^{-11} cm.^{3} molecule^{-1} sec.$^{-1}$ for the recombination of methyl radicals (8), and 3.9×10^{-11} cm.^{3} molecule^{-1} sec.$^{-1}$ for the recombination of trifluoromethyl radicals (1). There are some difficulties about the values for methyl radical reactions in Table II. A number of investigations, and particularly unpublished work by Kutschke and Whiteway (4), indicate that the value for the activation energy of $CD_3+CD_3COCD_3$ is higher than that previously reported (10). As a result the value for ethane (10) is too low, and has been corrected from 10.4 to 11.4 kcal. The value for C_3H_8 includes this correction. There is thus some inconsistency between the values for propane and those for n- and iso-butane. The latter compounds were investigated by a non-isotopic method, however, and are free from errors involving the reaction of CD_3 with CD_3COCD_3. As a result, until further work is done, there are uncertainties of the order of 1 kcal. in the values of activation energies for methyl radical reactions. The values of the rate constants at 400°K. are, however, affected very little by these uncertainties. Table II also shows for comparison some recent values obtained by

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Pritchard, Pritchard, and Trotman-Dickenson (6), using CF_3 radicals from the photolysis of hexafluoroazomethane. There is complete agreement between these values and those obtained with hexafluoroacetone. It will be seen from Table II that the abstraction of hydrogen from hydrocarbons by CF_3 radicals is about 100 times faster than the corresponding reaction of methyl radicals at 400°K. The activation energies for CF_3 reactions are 2–3 kcal. smaller than those for CH_3.

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THE POLYMERIZATION OF STYRENE IN THE PRESENCE OF α- AND β-BROMOSTYRENE[1]

By M. H. Jones

ABSTRACT

A study of the polymerization of styrene in the presence of either α- or β-bromostyrene at 45°C. and 70°C. has shown that copolymerization does not occur. From the variation of molecular weight and rate of polymerization with bromostyrene concentration it is concluded that the bromostyrenes behave essentially as efficient transfer agents.

INTRODUCTION

The bromination of polystyrene in solution, both photochemically and thermally, is accompanied by some degradation and there is evidence that the resultant polymer may contain olefinic bonds in the carbon chain due to the concomitant elimination of hydrogen bromide (6). As an alternative means of preparing polystyrenes containing aliphatic bromine atoms for use as polyradical sources in grafting experiments (5, 6), an attempt has been made to copolymerize styrene with α- or β-bromostyrene. This would permit a close control of the position and frequency of the bromine atoms in the polymer backbone and would avoid the disadvantages resulting from the direct bromination method.

Although the aliphatic bromostyrenes do not polymerize by a radical mechanism alone (7, 11), it was considered that they may take part in a copolymerization reaction if the principal cause of their low reactivity is steric hindrance imparted by the bulky bromine atom. This is expected to be less in a transition state involving only one species containing a bromine atom adjacent to the reaction center, as in the unsymmetrical propagation step of a copolymerization reaction, than in the normal polymerization involving two species containing bromine atoms. However, in experiments at 45°C. and 70°C., no evidence of copolymerization was obtained and the bromostyrenes appeared to behave as efficient transfer agents.

EXPERIMENTAL

Materials

Styrene (Eastman Kodak Practical Grade) was shaken with a 10% sodium hydroxide solution to remove the inhibitor, washed with distilled water, and dried over anhydrous calcium chloride. It was distilled under reduced pressure in a stream of nitrogen and the middle fraction, b.p. 51.3°C. at 27 mm. pressure, was used for the polymerization experiments. Prior to use, the monomer was given a bulb-to-bulb distillation in vacuum.

α-Bromostyrene was prepared by the elimination of hydrogen bromide from styrene dibromide. Styrene dibromide (0.1 mole) was shaken for 20 min. with

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Contribution from the Department of Chemistry, Ontario Research Foundation, Toronto 5, Ontario.

100 cc. of a 20% solution of potassium hydroxide in ethanol, the temperature being maintained below 20°C. The reaction mixture was poured into a large excess of ice-cold water and the oil separated and dried over anhydrous sodium sulphate. The product was distilled under reduced pressure in a stream of nitrogen, second fraction b.p. 77.0–77.2°C. at 9 mm.; $n_D^{22.5}$ 1.5868. The conditions described by Ashworth and Burkhardt (1) yielded a product consisting principally of phenyl acetylene.

β-Bromostyrene (Eastman Kodak Practical Grade) was purified in a similar manner to the α-compound, b.p. 85.0–85.1°C. at 7 mm.; $n_D^{22.5}$ 1.6063. As both the bromostyrenes were found to be sensitive to atmospheric oxidation, particularly the α-isomer, they were sealed in ampoules under vacuum and stored at −5°C.

α,α′-Azo-bis-isobutyronitrile was recrystallized twice from ethanol in the temperature range 30°–0°C. and dried under vacuum.

Procedures

Reaction mixtures of styrene and the required bromostyrene were thoroughly degassed on a high vacuum line and sealed in pyrex vessels at a pressure of 10^{-3}–10^{-4} mm. For experiments at 45°C., 1.0 gm./liter of α,α′-azo-bis-isobutyronitrile was used as initiator and the reactions were followed dilatometrically. The volume contraction – time curves were linear and the rates recorded in Table I were calculated on the assumption that polystyrene is the

TABLE I

POLYMERIZATION OF STYRENE WITH α- AND β-BROMOSTYRENE AT 45°C.
1.0 gm./liter of α,α′-azo-bis-isobutyronitrile used as initiator

Expt. No.	Bromostyrene	[Styrene], moles l.$^{-1}$	$\frac{[\text{Bromostyrene}]}{[\text{Styrene}]}$	Rate . 10^7 vol. contraction, moles l.$^{-1}$ sec.$^{-1}$	Rate . 10^7 polymer recovered, moles l.$^{-1}$ sec.$^{-1}$	$[\eta]_{25°C.}$, dl. gm.$^{-1}$	M_n
2	—	8.49	—	142	128	1.72	425,000
13	α	7.98	0.060		5.6		
5	α	6.07	0.353	5.5	0.3		
14	β	7.98	0.061	115	110	0.182	9,000
1	β	6.79	0.224	83	54	0.110	4,500
3	β	4.25	0.893	17	7.4		
4	β	1.82	3.23	3.9	0.1		

only product of polymerization and that no copolymerization occurs. Using the data of Patnode and Scheiber (9) for the densities of monomer and polymer respectively, a contraction in volume of 15.4% at 45°C. corresponds to 100% polymerization. In all cases, conversions were limited to less than 7%. The polymer was recovered by precipitation in a 30–40 volume excess of methanol, filtered, and dried to constant weight in vacuum at room temperature. The rates of polymerization at 45°C. and 70°C. were also determined from the weights of polymer recovered in this way.

Intrinsic viscosities were measured in benzene solution at 25°C. using a modified Ubbelohde type viscometer incorporating a bulb to permit dilution

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of the solutions *in situ*. No kinetic energy corrections were applied to the flow times as they were found to be less than 1%.

RESULTS AND DISCUSSION

The rates of polymerization for various styrene–bromostyrene compositions are recorded in Tables I and II together with the intrinsic viscosities of the

TABLE II

POLYMERIZATION OF STYRENE WITH α- AND β-BROMOSTYRENE AT 70°C.
No initiator used

Expt. No.	Bromo-styrene	[Styrene], moles $l.^{-1}$	$\frac{[\text{Bromostyrene}]}{[\text{Styrene}]}$	$k_2 . 10^7$, $l.\ moles^{-1}\ sec.^{-1}$	$[\eta]_{25°C.}$, $dl.\ gm.^{-1}$	M_n
10	—	8.29	—	0.875	3.26	740,000
18	α	8.18	0.012	0.103	0.166	8,000
17	α	7.78	0.059	0.040	0.087	3,000
6	α	5.53	0.448	0.030		
7	α	3.11	1.49	<0.005		
19	β	8.18	0.012	0.715	0.480	41,000
12	β	7.78	0.060	0.760	0.172	8,500
8	β	5.53	0.441	0.785	0.095	3,500
9	β	3.11	1.47	0.030		

products obtained. The molecular weights given in the last columns of these tables were calculated from the intrinsic viscosity – molecular weight relationship suggested by Pepper (10) for unfractionated polystyrenes in the molecular weight range 2.10^3–2.10^6,

$$\text{i.e. } [\eta] = 4.37.10^{-4}\ M_n^{0.66}.$$

Microanalyses of the products from reactions with high bromostyrene concentrations showed that they may contain as much as 4.5% bromine. However, the ultraviolet absorption curve of the polymer from experiment No. 8 had peaks at 2850 Å and 2950 Å which occur in the absorption spectrum of β-bromostyrene but are not present in those of either polystyrene or a brominated polystyrene prepared by direct bromination. Assuming the product to be a mixture of polystyrene and β-bromostyrene, the percentage composition of the latter was determined from the optical densities at various wave lengths in the region 2550–2950 Å. The analyses were constant within the experimental accuracy and were in good agreement with the value obtained from the microanalysis for bromine. Two reprecipitations of the polymer from benzene solution in methanol reduced the absorption attributed to the bromostyrene by a factor of two. That there can be incomplete separation of the polymer and bromostyrene by precipitation was demonstrated by a blank experiment in which a sample of pure polystyrene was recovered and dried in the normal way from a benzene solution containing 20% β-bromostyrene. The presence of the bromo compound was detected in the ultraviolet spectrum of the product. Although the bromostyrenes are soluble in methanol they are insoluble in solutions containing more than 5–10% water. Presumably condensation of

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atmospheric water vapor during filtration of the polymer under reduced pressure precipitates the bromostyrene which is then absorbed on the polymer. Because of its very low vapor pressure, it will not be completely removed when dried under vacuum at room temperature.

From the spectra of the products from experiments Nos. 1 and 8 it has been estimated that the true bromine contents are less than 0.7% and, consequently, there cannot be more than one bromostyrene unit in 110 units of the polymer chain, that is, in a molecular weight of approximately 11,000. As the molecular weights of these polymers from viscosity measurements are 4500 and 3500 respectively, they must contain less than one bromine atom per molecule. The bromine contents of the products from reactions with low bromostyrene concentrations, in which there was less contamination of the polymer by bromostyrene, were also lower than the requirement for one bromine atom per molecule. There is, therefore, no evidence that copolymerization occurs.

The rapid fall in molecular weight with increasing bromostyrene concentration, both for polymerizations at 45°C. and 70°C., suggests that the growing polymer radicals terminate by one or both of the following mechanisms.

(1) The addition of a bromostyrene molecule to a growing polymer chain produces a radical with a low reactivity towards propagation,

$$\underset{\text{Active}}{M_n^{\cdot}} + \text{B} \rightarrow \underset{\text{Inactive}}{M_n\text{B}^{\cdot}}$$

termination occurring by mutual interaction with a polystyrene radical or another of its own kind.

(2) The bromostyrenes act as efficient transfer agents,

$$M_n^{\cdot} + \text{B} \rightarrow M_n + \text{B}^{\cdot}.$$

With the catalyzed reactions at 45°C., where the rate of initiation is constant, there should be an exact correspondence between the decrease in molecular weight and the fall in rate of polymerization for mechanism (1), provided transfer to monomer is small and can be neglected (2). For the thermal reactions at 70°C., in which transfer to monomer is an important termination step, it can be shown that this mechanism requires the proportional decrease in molecular weight to be less than the decrease in the second order rate constant k_2, where $k_2 = \text{rate}/[\text{M}]^2$. It is generally accepted that the rate of initiation for uncatalyzed thermal polymerizations is proportional to the square of the monomer concentration. For reactions with both the β-isomer at 45°C. and the α- and β-isomer at 70°C., the fall in molecular weight is at least 20 times greater than required for these relationships (Tables I and II). Thus, the addition of a bromostyrene molecule to form an inactive radical is not the predominant chain termination process.

Although the reaction rates determined dilatometrically and from the polymer recovered are not strictly comparable, particularly for reactions with high bromostyrene concentrations, the trend is similar. It is probable that the greater rate decrease obtained by the second method is attributable to incomplete precipitation of low molecular weight material which is progressive as the

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molecular weight decreases. Confirmation of this was obtained in two of the experiments at 70°C. (Nos. 7 and 9) in which 50% of each reaction mixture was transferred to a distillation apparatus, degassed, sealed under vacuum, and the volatile constituents removed in a bulb-to-bulb distillation. In both cases, gummy residues remained which consisted of very short chain polymers as they were partly soluble in methanol and readily soluble in acetone. This partial fractionation will also mean that the true molecular weights are somewhat less than the determined values in the low molecular weight range.

If the bromostyrenes act principally as transfer agents and the radicals formed in the transfer step are equally efficient in continuing polymerization, then, for the initiated reactions with a constant catalyst concentration, the rate of polymerization will be proportional to the monomer concentration. For the thermal reactions without initiator, the dependence will be second order with respect to monomer concentration, that is, k_2 will remain constant (3, 4). Although the rate measurements are not too precise, the rates as a function of monomer concentration are less than for first and second order relationships, which suggests that the probability of the radicals resulting from transfer continuing the kinetic chain is less than unity. This is particularly apparent for reactions with α-bromostyrene at 70°C. but the evidence for reactions with the β-isomer at the same temperature is not conclusive. In addition, it must be recognized that a similar effect would be observed in the catalyzed reactions if the bromostyrenes compete with the monomer for the initiator fragments, since this will cause a progressive reduction in the rate of starting chains. Transfer constants for the two bromo compounds have been determined from the variation of molecular weight with bromostyrene–styrene ratio (8). Although this method is strictly applicable only when each radical formed by transfer continues polymerization, it has been used to obtain approximate values. At 70°C., the transfer constants for the α- and β-bromostyrene are 1.0 and 0.2 and are respectively 100 and 20 times greater than that of carbon tetrachloride at this temperature (4).

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THE PHOTOLYSIS OF KETENE IN THE PRESENCE OF HYDROGEN[1]

By H. Gesser[2] and E. W. R. Steacie

ABSTRACT

The photolysis of ketene in the presence of hydrogen has been investigated in the temperature range −40° to 207°C. The main products are CO, C_2H_4, C_2H_6, and CH_4, with some methyl ethyl ketone at the higher temperatures. Hydrogen and ketene compete for CH_2 radicals by the reactions

$$CH_2 + CH_2CO \rightarrow C_2H_4 + CO \quad [2]$$

$$CH_2 + H_2 \rightarrow CH_3 + H \quad [3]$$

with $E_3 - E_2 = 0.8$ kcal. At the higher temperatures the reaction

$$CH_3 + H_2 \rightarrow CH_4 + H \quad [6]$$

leads to a chain reaction via

$$H + CH_2CO \rightarrow CH_3 + CO. \quad [4]$$

The value of E_6 is found to be 10.2±0.5 kcal. in good agreement with previous work.

INTRODUCTION

The recent study by Strachan and Noyes (10) of the photolysis of ketene and ketene–oxygen mixtures has greatly clarified the mechanism of the ketene photolysis and its dependence on wave length. In view of this it was believed that a re-examination of the ketene–hydrogen system, previously investigated by Rosenblum (7, 8), would perhaps distinguish unambiguously between the addition (1) and abstraction (8) reactions of CH_2 radicals with hydrogen.

Bawn and Milsted (1) studied the reaction of sodium atoms with the methylene halides and found that at 300°C. with hydrogen as the carrier gas CH_4 was the principal product, whereas with nitrogen as the carrier gas C_2H_4 was the main hydrocarbon product. They therefore postulated the reaction

$$CH_2 + H_2 \rightarrow CH_4. \quad [3a]$$

Rosenblum (8), however, postulated

$$CH_2 + H_2 \rightarrow CH_3 + H \quad [3]$$

to account for the high proportion of saturated hydrocarbons produced by the photolysis of ketene in the presence of hydrogen.

During the course of this investigation Chanmugam and Burton* (2) studied the photolysis of ketene in the presence of hydrogen and deuterium from 27° to 412°C. They conclude that reaction [3*a*] occurs to a small extent at 27° and has a low activation energy, while [3] only occurs at higher temperatures.

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Contribution from the Division of Pure Chemistry, National Research Council, Ottawa, Canada. Issued as N.R.C. No. 3835.
[2]*National Research Council of Canada Postdoctorate Fellow 1954–55. Present address: Department of Chemistry, University of Manitoba, Winnipeg, Manitoba.*
**We are greatly indebted to Drs. Burton and Chanmugam for allowing us to see the manuscripts of their papers prior to publication.*

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EXPERIMENTAL

The apparatus, essentially completely free of stopcocks, was similar to that of Strachan and Noyes (10). It consisted of a quartz cell 5 cm. in diameter and 10 cm. long enclosed in an insulated box which served as an air oven. The temperature was controlled by means of a mercury regulator to within $\pm 2°$ at temperatures above room temperature. A few experiments were performed at $-40°$C. by partial filling of the box with dry ice. Under these circumstances there was a slight amount of condensation on the quartz windows of the box which caused small variations in the intensity of illumination. The volume of the cell was 193 cm.^{3}, and the total volume of cell and connecting tubing was about 225 cm.^{3}.

The analytical units consisted of a furnace containing copper and copper oxide maintained at 210°C. for the analysis of CO, H_2, CH_4 mixtures, a hydrogenator (9) for the analysis of C_2H_4, C_2H_6 mixtures, and a platinum wire unit for the combustion of CH_4. The CO, H_2, CH_4 fraction was separated at $-215°$C., and the C_2 fraction at $-185°$C. by means of a LeRoy still.

Ketene was prepared by the thermal decomposition of acetic anhydride (4) at 500°C. It was degassed repeatedly at the temperature of liquid oxygen, and distilled from a trap at $-130°$C. into a bulb where it was stored in liquid nitrogen. When the ketene was allowed to react with acetic acid, CO_2 was detected as an impurity, present in the ketene to the extent of 0.1%.

Hydrogen was purified by passage of commercial cylinder hydrogen through three traps immersed in liquid nitrogen and through two palladium thimbles maintained at 320°C. Its purity was tested by means of the copper oxide furnace. It was found that approximately 0.0002% of the hydrogen did not disappear to form water in the presence of hot copper oxide. Traces of CO and CH_4 were found, and the yields of the products were corrected for them. Hydrogen was stored in a 5 liter bulb and was dosed into the cell by means of a 100 cc. mercury Toepler pump, with the ketene previously measured and frozen down with liquid nitrogen. The gases were then allowed to mix by warming to room temperature and repeated expansion into the Toepler pump.

The light source was a Hanovia S-500 medium-pressure mercury arc, collimated by means of two quartz lenses. The almost parallel beam was allowed to fill the cell. The intensity was checked by means of a General Electric type GL 935 phototube. The light was filtered with a Corning glass filter No. 9863 (3 mm.) and a chlorine filter in quartz (5 cm. long at 1 atm. pressure). The effective absorbed radiation was thus about 2700 Å, with about six per cent above 3600 Å. The intensity was varied by means of neutral density filters of aluminum sputtered on quartz.

RESULTS

The products of the photolysis of ketene in the presence of hydrogen at $-40°$ and 26°C. were CO, C_2H_4, and C_2H_6, together with some polymer detected by a slow drop in the transmission of the cell windows. The cell was occasionally flamed with half an atmosphere of oxygen to remove the polymer. At higher temperatures CH_4 was also produced. Experiments at 26°C. showed that the

TABLE I

PHOTOLYSIS OF KETENE–HYDROGEN MIXTURES

Illumination time = 1 hr.

$[CH_2CO]$	$[H_2]$	R_{CO}	$R_{C_2H_4}$	$R_{C_2H_6}$	R_{CH_4}	$\frac{R_{CO}}{R_{C_2H_4}}$	Material balance	R_{MEK}
molecules/cc. $\times 10^{-18}$		molecules/cc./sec. $\times 10^{-13}$						molecules/cc./sec. $\times 10^{-13}$
			Temperature = -40 ± 4°C.					
0.83	2.49	.304	.080	.069	—		.980	
0.81	6.86	.258	.039	.092	—		1.016	
0.81	—	.315	.140			2.25		
0.83	4.56	.247	.045	.076	—		.980	
			Temperature = 26 ± 2°C.					
0.97	—	.594	.272			2.18		
0.97	1.62	.590	.170	.118	—		.976	
0.97	0.97	.571	.183	.091	—		.960	
0.97	0.36	.583	.232	.037	—		.923	
0.97	3.60	.535	.100	.161	—		.976	
1.00	—	.428	.194			2.21		
1.00	6.36	.409	.061	.145	—		1.007	
0.98	4.79	.416	.067	.130	—		.947	
0.95	—	.387	.174			2.22		
1.00	3.78	.412	.078	.117	—		.947	
0.97	1.91	.392	.098	.092	—		.969	
0.97	1.01	.377	.125	.060	—		.981	
0.94	—	.361	.161			2.24		
1.68	1.29	.598	.214	.070	—		.950	
1.65	0.78	.577	.228	.048	—		.957	
1.62	0.61	.549	.226	.037	—		.958	
			Temperature = 99 ± 2°C.					
1.36	0.55	.571	.217	.037	.003		.895	
1.32	0.86	.563	.191	.059	.005		.897	
1.27	2.02	.558	.136	.104	.016		.889	
0.84	2.66	.463	.076	.106	.026		.842	
0.81	3.82	.446	.054	.129	.039		.908	
0.71	6.00	.401	.028	.131	.059		.940	
			Temperature = 149 ± 2°C.					
0.68	4.90	.549	.031	.083	.216		.809	.052
0.71	3.87	.522	.036	.084	.172		.789	.055
0.69	3.16	.508	.043	.085	.140		.780	.056
0.68	—	.354	.159			2.23		
1.17	—	.572	.251			2.28		
1.14	3.25	.735	.101	.089	.152		.724	.101
0.92	—	.454	.197			2.30		
0.89	1.49	.515	.104	.066	.058		.773	.058
1.03	—	.489	.212			2.31		
1.01	0.66	.512	.155	.034	.020		.777	.057
0.48	—	.234	.103			2.27		
0.48	1.81	.293	.027	.062	.064		.826	.026
0.92	—	.410	.183			2.24		
0.92	3.25	.590	.060	.091	.145		.758	.071
0.69	—	.405	.178			2.28		
0.69	2.41	.478	.066	.074	.111		.818	.043
			Temperature = 207 ± 2°C.					
0.49	4.59	1.00	.057	.056	.636		.862	.069
0.48	—	.260	.106			2.45		
0.50	3.66	.846	.059	.053	.488		.842	.067
0.52	2.25	.676	.065	.054	.297		.791	.070
1.03	—	.524	.215			2.44		
1.01	2.25	1.03	.169	.048	.285		.698	.155
1.01	1.31	.813	.182	.030	.139		.693	.125

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addition of hydrogen to ketene undergoing photolysis had no effect on R_{CO} (the rate of formation of CO). However, at higher temperatures where CH_4 was produced, the addition of hydrogen to ketene caused an increase in R_{CO} such that R_{CO} for ketene alone was about equal to $R_{CO}-R_{CH_4}$ for ketene–hydrogen mixtures.

Mass spectrometric analysis showed that in experiments with ketene alone up to 207°C. the CO fraction contained less than 0.5% methane, and the C_2H_4 fraction contained less than 0.5% ethane with no detectable amounts of acetylene. The yields of CO_2 were always negligible compared with the impurity already present in the ketene.

In experiments at 149° and 207°C. relatively large amounts of products were obtained which were volatile above 125° and were not found in comparable quantities in the absence of hydrogen or at lower temperatures (except at 99°C. at very low intensities). Mass spectrometric analysis of this fraction showed that the gases volatile between −75° and −125°C. contained from 30 to 50% methyl ethyl ketone. The remaining gases which could not be positively identified were probably other mixed ketones.

The extent of decomposition was usually about two per cent, except at the highest temperatures where, because of the chain reaction, the decomposition was about six per cent under similar conditions.

The rates of formation of products are given in Table I. Table II shows the effect of intensity (a variation of about 500-fold). The filter used in this series

TABLE II

EFFECT OF INTENSITY

$[CH_2CO]$ molecules/cc. $\times10^{-18}$	$[H_2]$	Temp., °C.	Relative intensity	Time, sec.	R_{CO}	$R_{C_2H_4}$	$R_{C_2H_6}$	R_{CH_4}	$\frac{R_{CO}}{R_{C_2H_4}}$	Material balance
					molecules/cc./sec. $\times10^{-12}$					
1.16	—	26	1000	500	17.02	7.52			2.26	
1.08	2.16	26	1000	200	17.21	5.40	3.10	—		.992
1.07	2.13	26	14	7000	0.267	0.071	0.058	—		.966
1.03	—	26	14	7000	0.263	0.117			2.25	
0.92	1.79	99	1000	100	18.10	4.43	4.28	—		.964
0.91	1.79	99	14	6900	0.289	0.060	0.064	0.011		.896
0.90	—	99	14	7200	0.277	0.128			2.16	
0.95	1.88	99	2	54000	0.0333	0.00622	0.00475	0.00373		.771
0.93	—	99	2	54000	0.0290	0.0129			2.25	
0.80	2.57	149	1000	60	14.08	2.24	4.21	0.960		.984
0.79	—	149	1000	60	13.83	6.29			2.20	
0.80	2.67	149	2	54000	0.0464	0.00432	0.00310	0.0163		.671
0.78	—	149	2	54000	0.0240	0.0102			2.35	

NOTE: *A dash signifies product not detectable.*
A blank space indicates that no analysis was made.

was a Corning No. 9863 alone, giving effective radiation from 3900 Å to 2600 Å. Experiments at 26°C. with ketene–hydrogen mixtures using 3660 Å and 3130 Å gave results similar to those with 2700 Å.

One experiment was performed at shorter wave lengths in which 54 mm. of ketene at 26°C. was photolyzed with the 2139 Å line of a low pressure zinc resonance lamp, the longer wave length resonance line 3076 Å being removed by means of a chlorine filter. The products were mainly CO and C_2H_4, and were analyzed by means of a mass spectrometer. The CO fraction was shown

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to contain 0.75% H_2, and the C_2 fraction had the following composition: 3.5% C_2H_2, 5.4% C_2H_6, 91.1% C_2H_4. The value of $R_{CO}/R_{C_2H_4}$ was 2.38. There are thus small but definite differences as compared with the results at longer wave lengths, possibly owing to the onset of another primary process.

DISCUSSION

Consideration of the principal products of the photolysis of ketene in the presence of hydrogen leads to the following material balance:

$$(2R_{C_2H_4}+2R_{C_2H_6}+R_{CH_4})/R_{CO} = 1.$$

The values of this ratio are given in Tables I and II under the heading "Material balance". It is evident that the material balance decreases with increase in temperature (Table I), and increases with increase in intensity (Table II). Some polymerization occurred, and this resulted in a slight decrease in transmission in successive runs. This is reflected in the values of R_{CO} in Table I, but the ratios of rates are not affected. In view of the large variation in intensity in Table II, no appreciable error is involved in conclusions regarding the effect of intensity. The small increase in the ratio $R_{CO}/R_{C_2H_4}$ with increase in temperature is probably due to an increase in the amount of polymer formed at higher temperatures. The values of the material balance show that polymerization is never of major importance, especially at low temperatures.

The mechanism most consistent with our results is as follows:

$$CH_2CO + h\nu \rightarrow CH_2 + CO \quad [1]$$

$$CH_2 + CH_2CO \rightarrow C_2H_4 + CO \quad [2]$$

$$CH_2 + H_2 \rightarrow CH_3 + H \quad [3]$$

$$H + CH_2CO \rightarrow CH_3 + CO \quad [4]$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \quad [5]$$

$$CH_3 + H_2 \rightarrow CH_4 + H \quad [6]$$

If ethane and methane are produced solely by reactions [5] and [6], then the following relation should be obeyed:

$$R_{CH_4}/R^{\frac{1}{2}}_{C_2H_6} = k_6[H_2]/k_5^{\frac{1}{2}}. \quad [I]$$

Fig. 1 shows a plot of $R_{CH_4}/R^{\frac{1}{2}}_{C_2H_6}$ against $[H_2]$ at 99°, 149°, and 207°C. and it is evident that the above relationship is obeyed. The values of $k_6/k_5^{\frac{1}{2}}$ at the different temperatures were obtained from the slopes of the curves in Fig. 1, and are given in Fig. 2 in the form of an Arrhenius plot. The values of $k_6/k_5^{\frac{1}{2}}$ reported by Majury and Steacie (6) from an investigation of the photolysis of acetone–hydrogen mixtures are given for comparison. The agreement is excellent except at the highest temperature where Majury and Steacie's results are unreliable. The results of the present work lead to the expression

$$13+\log k_6/k_5^{\frac{1}{2}} = 5.96-(2.24\times10^3/T),$$

and to $E_6-\frac{1}{2}E_5 = E_6 = 10.2\pm0.5$ kcal. This agrees well with the value re-

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ported by Whittle and Steacie (11) of 10.0±0.5 kcal. If collision diameters of 2.8 Å and 3.5 Å are assumed for H_2 and CH_3, the ratio of the steric factors, $P_6/P_5^{\frac{1}{2}}$, is 2.3×10^{-3}. The complete agreement with previous work is strong

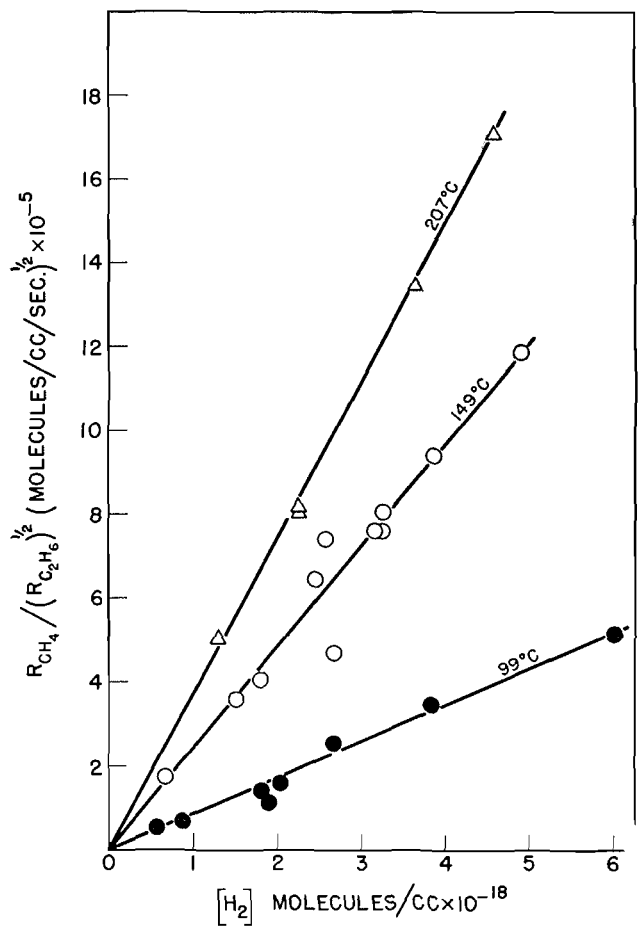

FIG. 1. Plot of $R_{CH_4}/R_{C_2H_6}^{\frac{1}{2}}$ against $[H_2]$. For convenience in plotting, the values of the ordinate have been divided by 2 for the 149°C. curve, and by 5 for the 207°C. curve.

evidence that reaction [3*a*] is unimportant as a source of methane in the present work. This is to be expected from the work of Chanmugam and Burton (2) who showed that at 27°C. the total methane, amounting to about one per cent of the CO, is formed by reaction [3*a*], whereas at higher temperatures the methane is predominantly formed by a radical reaction.

A mechanism involving reactions [1] to [6] leads to the relationship:

$$R_{C_2H_6}/R_{C_2H_4} = k_3[H_2]/k_2[CH_2CO]. \qquad [II]$$

A plot of $R_{C_2H_6}/R_{C_2H_4}$ against $[H_2]/[CH_2CO]$ is shown in Fig. 3. The slopes of the lines, corresponding to k_3/k_2, are 0.28, 0.40, and 0.52 for −40°, 26°, and 99°

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respectively. An Arrhenius plot of these values is given in Fig. 4, whence $E_3 - E_2 = 0.8$ kcal., and $P_3/P_2 \sim 1$.

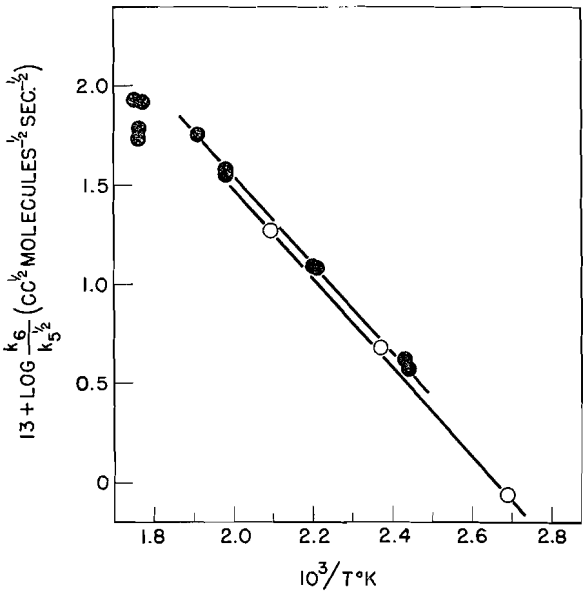

FIG. 2. Arrhenius plot of $k_6/k_5^{\frac{1}{2}}$. Open circles represent the present work. The filled circles are from the work of Majury and Steacie.

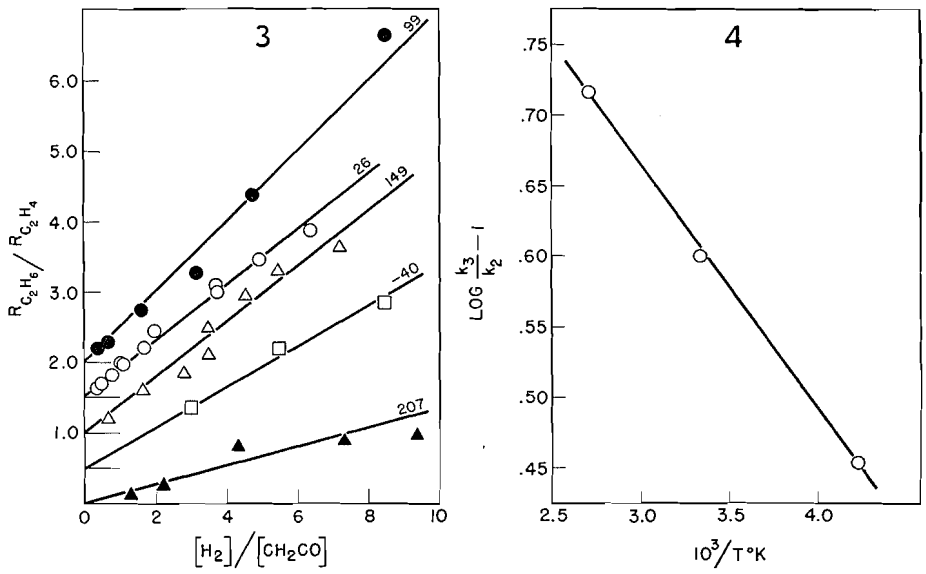

FIG. 3. Plot of $R_{C_2H_6}/R_{C_2H_4}$ against $[H_2]/(CH_2CO]$. The temperatures are indicated by the numbers on the lines. For clarity, the origin of each successive curve is displaced upwards by increments of 0.5 units.

FIG. 4. Arrhenius plot of k_3/k_2 from data in Fig. 3.

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At 99°C. appreciable methane is formed, and it is possible to check both equations [I] and [II]. The results agree excellently. It follows that a reaction sequence such as

$$CH_2 + CH_2CO \rightarrow CH_2CH_2CO$$
$$CH_2CH_2CO + H_2 \rightarrow C_2H_6 + CO,$$

as postulated by Chanmugam and Burton to account for the formation of ethane at 27°C., cannot be of any importance in the present work even at low temperatures.

The slopes of the lines in Fig. 3 give an excellent Arrhenius plot at the three lowest temperatures. At higher temperatures, however, the slopes decrease again, being 0.40 at 149° and 0.13 at 207°. Also, the plot in Fig. 3 is far from linear at 207°. The decrease in the apparent value of k_3/k_2 is almost certainly due to the formation of methyl ethyl ketone in view of the fact that both k_3/k_2 and the material balance (Table II) increase with increase in intensity. Methyl ethyl ketone presumably arises by the reactions

$$CH_3 + CH_2CO \rightarrow CH_2COCH_3 \qquad [7]$$
$$CH_3 + CH_2COCH_3 \rightarrow C_2H_5COCH_3. \qquad [8]$$

The rate of formation of methyl ethyl ketone, R_{MEK}, at 149° and 207°C. can be calculated by assuming that the material balance differs from unity solely because of the formation of methyl ethyl ketone. Hence $R_{MEK} = \frac{1}{2}R_{CO}$ (1 − material balance). The values thus calculated are given in Table I, and should obey the relationship

$$R_{CH_4}/R_{MEK} = k_6[H_2]/k_7(CH_2CO]. \qquad [III]$$

Fig. 5 shows that this relationship is obeyed satisfactorily. The slopes lead to $E_6 - E_7 = 3.8$ kcal., i.e. $E_7 = 6.4$ kcal., and to $P_6/P_7 = 30$ or $P_7 = 7 \times 10^{-5}$. Since these values are derived from results at two temperatures only, and involve rather drastic assumptions, they are to be regarded as correct in magnitude only.

It is, however, possible to obtain some confirmatory evidence from the work of Chanmugam and Burton (3). Their work on the photolysis of ketene–acetone mixtures showed that methyl ethyl ketone was an important product. From their yields of methane and ethane it can be shown that at the three highest temperatures used by them (200°, 298°, and 412°C.) an Arrhenius plot of

$$R_{CH_4}/R^{\frac{1}{2}}_{C_2H_6}[\text{Acetone}]$$

gives an activation energy of 9.8 kcal. for reaction [9].

$$CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_2COCH_3. \qquad [9]$$

This is in excellent agreement with their own (3) and previous work on the acetone photolysis. It follows therefore that either all methane comes from [9] or that if CH_3 radicals abstract hydrogen from ketene the activation energy must also be approximately 9.8 kcal. This latter alternative is ruled out, however, by the fact that R_{CH_4} is a function of $[H_2]$ and is independent of $[CH_2CO]$ in the present work.

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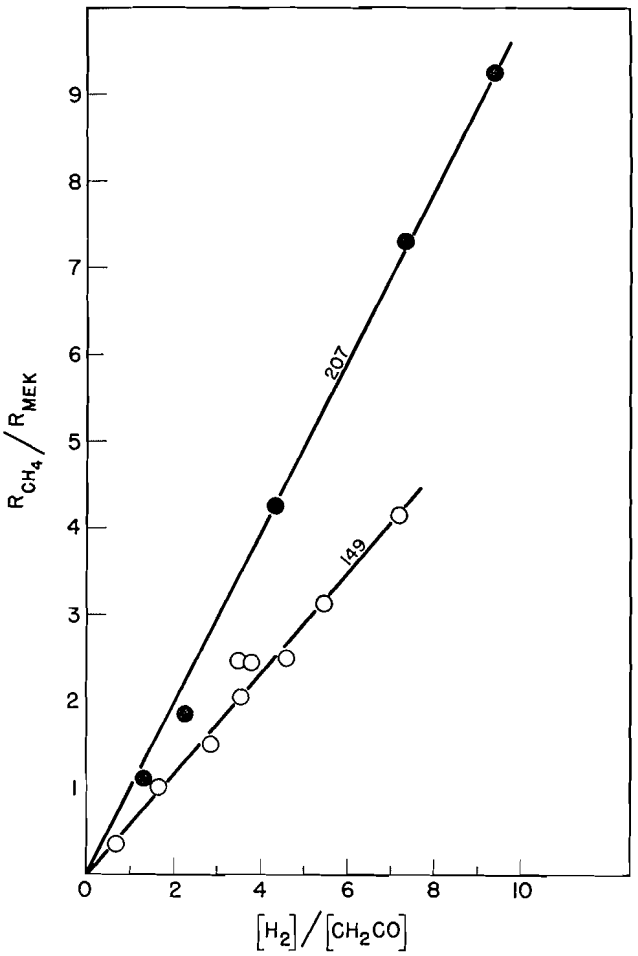

FIG. 5. R_{CH_4}/R_{MEK} plotted against $[H_2]/[CH_2CO]$. The temperatures are indicated on the curves.

If it is now assumed that [7] and [8] are the main method of forming methyl ethyl ketone (which is also assumed by Chanmugam and Burton) then an Arrhenius plot of

$$R_{CH_4}[CH_2CO]/R_{MEK}[\text{Acetone}]$$

using the results of Chanmugam and Burton leads to

$$E_9 - E_7 = 4.8 \text{ kcal.}, \qquad E_7 = 5 \text{ kcal.}$$

Considering the assumptions involved this is in excellent agreement with the value of 6.4 kcal. from the present work.

If equation [II] is now corrected to include reactions [7] and [8],

$$(R_{C_2H_6} + R_{MEK})/R_{C_2H_4} = k_3[H_2]/k_2[CH_2CO]. \qquad [IV]$$

Using equation [IV], we can correct the results in Fig. 3 for 149° and 207°C.

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In this way k_3/k_2 at 149° is raised to 0.66 in good agreement with the value of 0.59 obtained by extrapolation from Fig. 4. However, the results for 207° do not agree with equation [IV], since a straight line is not obtained when $(R_{C_2H_6}+R_{MEK})/R_{C_2H_4}$ is plotted against $[H_2]/[CH_2CO]$. Also, apart from the deviation from linearity the slope of the curve is much too small. A possible explanation is the formation of ethylene at the highest temperature by some process other than reaction [2], analogous to the unexplained formation of ethylene in the acetone photolysis at high temperatures.

In view of the uncertainties at the higher temperatures the exact value obtained for E_3-E_2 is open to some suspicion. There appears to be no doubt, however, that the difference between E_3 and E_2 is small.

The effect of intensity is in general agreement with the proposed mechanism. The competition between reactions [5] and [7] adequately explains the increase in the material balance, and the parallel increase in the apparent ratio k_3/k_2 as determined by equation [II] with increase in intensity.

Reaction [4] has previously been postulated by Knox, Norrish, and Porter (5) to account for the chain decomposition in the flash photolysis of ketene. To gain further evidence for its occurrence it was desirable to use a system in which hydrogen atoms were produced in the presence of ketene. With this in view an experiment was performed in which a 4:1 H_2–CH_2CO mixture was saturated with mercury vapor and illuminated with mercury resonance radiation (2537 Å) at 26°. Under these circumstances CH_4 was not formed, and the material balance was 1.0. The ratio $R_{C_2H_6}/R_{C_2H_4}$ was 4.2, about 2.5 times greater than that obtained for the photolysis of an equivalent mixture at 2700 Å. This is strong evidence for the occurrence of reaction [4].

The mechanism leads to $E_3-E_2 = 0.8$ kcal. All indications are that E_2 is small. Hence E_3 is of the order of 3 kcal. For reaction [3]

$$-\Delta H_3 = D(CH_2-H)-D(H-H)$$

$$= D(CH_2-H)-103 \text{ kcal.}$$

Hence E_3 can only be as small as 3 kcal. if $D(CH_2-H)$ is at least 100 kcal. If the high value of the latent heat of the sublimation of carbon, $L_C = 170$ kcal., is correct, as seems almost certainly to be the case, such a value for $D(CH_2-H)$ is reasonable. Recent unpublished work by Kistiakowsky in fact indicates that $D(CH_2-H)$ is probably greater than $D(CH_3-H)$.

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AN OXYGEN-18 STUDY OF ACETAL FORMATION AND HYDROLYSIS[1]

By Fred Stasiuk,[2] W. A. Sheppard,[3] and A. N. Bourns

ABSTRACT

A tracer study has been made of acetal formation and hydrolysis. Benzaldehyde and *n*-butyraldehyde, enriched in O^{18}, on reaction with *n*-butyl and allyl alcohols, gave acetals of normal isotopic abundance. The label appeared in the water of condensation. Hydrolysis of benzaldehyde di-*n*-butyl acetal and *n*-butyraldehyde di-*n*-butyl acetal in O^{18} enriched water gave alcohols of normal isotopic content. A slight enrichment due to isotopic exchange was found in allyl alcohol produced by the hydrolysis of benzaldehyde diallyl acetal. These results establish that the reversible reaction proceeds by a fission of the aldehyde-carbon to oxygen bond.

INTRODUCTION

The rate-determining step in the acid-catalyzed formation of an acetal from aldehyde and alcohol is generally assumed to be the reaction of the second alcohol molecule with the conjugate acid of an intermediate hemiacetal. In the reverse of this reaction, that is, in acetal hydrolysis, the formation of the hemiacetal from the conjugate acid of the acetal is considered to be the slow step (4).

On the basis of the relative hydrolysis rates observed for a number of formaldehyde acetals (12), Hammett has suggested a unimolecular mechanism in which there is formed a carbonium ion intermediate derived from the alcohol component of the molecule (4).

$$[RCH(OR')—OHR']^+ \xrightarrow{\text{slow}} RCHOR'—OH + [R']^+$$

$$[R']^+ + H_2O \xrightarrow{\text{fast}} [R'OH_2]^+$$

Hydrolysis rates, however, are much more sensitive to structural changes in the aldehyde component. For example, the following relative rates have been observed in the hydrolysis of acetals of pentaerythritol: formaldehyde, 1; acetaldehyde, 6×10^3; acetone, 1×10^7 (13). Ingold (5) has pointed out that this kinetic effect can be understood if the carbonium ion is derived from the aldehyde component since then the methyl substituents would be joined directly to the electron deficient carbon.

$$[RCH(OR')—OHR']^+ \xrightarrow{\text{slow}} [RCHOR']^+ + R'OH$$

$$[RCHOR']^+ + H_2O \xrightarrow{\text{fast}} [RCH(OR')—OH_2]^+$$

This mechanism also accounts for the markedly greater ease of hydrolysis of acetals compared to ordinary ethers.

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Contribution from the Department of Chemistry, Hamilton College, McMaster University, Hamilton, Ontario. Presented before Section III, Royal Society of Canada, Kingston Meeting, June, 1950.

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In acetal formation these reactions would be reversed with carbon–oxygen bond fission giving a carbonium ion again being the slow step.

The use of oxygen-18 provides a means of distinguishing between the two mechanisms since the oxygen appearing in the product, water, from acetal formation or in the product, alcohol, from acetal hydrolysis would have a different origin in the two cases. Benzaldehyde and *n*-butyraldehyde, enriched in O^{18}, have been reacted with *n*-butyl alcohol and allyl alcohol, and the O^{18} content of the resulting acetals and of the water of condensation determined for each of the four reaction systems. Allyl alcohol was chosen as an alcohol reactant since resonance stabilization of the allyl carbonium ion might be expected to provide a system most favorable for reaction by the Hammett mechanism. Hydrolysis in O^{18} enriched water of three acetals, benzaldehyde di-*n*-butyl acetal, *n*-butyraldehyde *n*-butyl acetal, and benzaldehyde diallyl acetal, has also been studied. The alcohol product was isolated and its oxygen isotopic abundance determined.

After the present investigation had been completed, O'Gorman and Lucas (9) reported a stereochemical study of acetal hydrolysis in which the acetal of D(+)-2-octanol was hydrolyzed to give D(+)-2-octanol of the same rotation as the original alcohol from which the acetal had been prepared. Since reaction by the Hammett mechanism would be expected to give extensive racemization, these authors conclude that it is the aldehyde carbon which forms the carbonium ion.

EXPERIMENTAL

Preparation of Benzaldehyde-O^{18} and Butyraldehyde-O^{18}

The aldehydes were shaken for three days with O^{18} enriched water containing approximately 0.8 atom % (0.6 atom % excess) of the heavier isotope. Water was separated and the aldehydes dried by azeotropic distillation with benzene. Their O^{18} content was determined in two ways: (1) by calculation from a knowledge of the O^{18} content of the water before and after equilibration, and (2) by determining the O^{18} content of the water produced on reaction of the aldehyde with phenylhydrazine under conditions which permitted its continuous removal by azeotropic distillation with benzene. Although there was good agreement between the two methods, the values obtained by the second have been used in Table I, since similar techniques were used in determining the O^{18} content of the water produced in acetal synthesis.

Acetal Formation

Carefully dried alcohol (0.32 mole) and the O^{18} enriched aldehyde (0.16 mole) were dissolved in 50 ml. of dry benzene and 0.5 gm. of anhydrous *p*-toluenesulphonic acid added. The solution was refluxed gently with continuous removal of the water of condensation using a Dean-Stark separator. The resulting acetal was recovered in the usual way, distilled, and converted to water and hydrocarbon in the manner described below.

Acetal Hydrolysis

The acetal (0.11 mole), enriched water (0.5 mole) containing approximately 0.4 atom % excess O^{18}, and two drops of concentrated hydrochloric acid were

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shaken together for two hours in a stoppered flask at 60–70° C. After the reaction mixture was cooled, it was neutralized with sodium hydroxide solution, water separated, and the alcohol product isolated by fractional distillation. The alcohol was dried azeotropically with benzene and converted to water and hydrocarbon by hydrogenolysis.

Hydrogenolysis of Organic Compounds and Mass-spectrometric Analysis of the Oxygen Isotopes

The acetals and alcohols were passed with a stream of dry hydrogen at 400° C. over a thoria-promoted nickel catalyst (11). Water, formed in 60-80% yields, was purified by distillation, and its O^{18} content determined by equilibration with carbon dioxide followed by a mass-spectrometric analysis of the oxygen isotopes in the carbon dioxide (3). The water removed azeotropically in the reaction of the aldehydes with phenylhydrazine and in acetal formation was purified by distillation over small quantities of sodium hydroxide and potassium permanganate before equilibration with carbon dioxide. Corrections were made for O^{18} dilution resulting from oxygen exchange with these compounds.

The isotopic analyses were made using a 180° direction-focusing Nier type mass spectrometer equipped with an automatic recorder (7). The precision of the mass-spectrometric analyses was $\pm 0.1\%$, while the over-all precision was considerably poorer, about ± 2–3%, owing to small and variable dilution of O^{18} during manipulative procedures.

Tests for Oxygen Exchange between Reactants and Products

Since exchange of oxygen between aldehyde and alcohol or acetal under the conditions of acetal synthesis would destroy the significance of the results insofar as mechanism considerations are concerned, the following tests for exchange were carried out:

(*a*) A synthesis of benzaldehyde di-*n*-butyl acetal using benzaldehyde containing 0.316 atom % excess O^{18} was carried to half completion, the unreacted *n*-butyl alcohol was separated, purified, and converted to water by hydrogenolysis, and the O^{18} content of the water determined in the manner previously described. The enrichment of the alcohol was found to be only 0.012 atom %.

(*b*) A benzaldehyde di-*n*-butyl acetal synthesis from benzaldehyde containing 0.346 atom % excess O^{18} was carried to half completion, the unreacted aldehyde and the acetal each separated, purified, and converted to water by methods already described. The benzaldehyde was found to contain 0.324 atom % excess, while the acetal was normal.

It is apparent from these results that, under the conditions used in the tracer study of acetal formation, there were no significant complications arising from exchange between normal and enriched materials.

Acid-catalyzed exchange between water and *n*-butyl alcohol during acetal hydrolysis experiments would certainly be too slow to appreciably affect the results (10, 2). Allyl alcohol, however, might be expected to undergo exchange much more rapidly and, therefore, an experiment was made to determine the extent of such exchange under the conditions used in the tracer studies. Allyl

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alcohol, containing the normal abundance of the oxygen isotopes, was dissolved in five molar equivalents of water, containing 0.444 atom % excess O^{18}, and the solution maintained at 65° C. for two hours. At the end of this period the alcohol was isolated, carefully dried, converted into water, and the oxygen isotopic abundance determined in the usual way. The alcohol was found to contain 0.018 atom % excess O^{18}, showing that, although there was some exchange, it was not sufficiently rapid to invalidate conclusions based on the results of the tracer work.

RESULTS AND DISCUSSION

The results of the tracer study of acetal formation for the four different systems of aldehyde plus alcohol are shown in Table I. In each case, the acetal formed from the O^{18} enriched aldehyde has been found, within experimental error, to have the normal abundance of the oxygen isotopes. With the exception of the reaction of benzaldehyde with *n*-butyl alcohol, however, not all of the

TABLE I

OXYGEN-18 RESULTS FOR ACETAL FORMATION

Acetal	Isotopic abundances (atom % excess)*			% of excess O^{18} reappearing in water
	Original aldehyde	Water of condensation	Acetal	
Benzaldehyde (1) di-*n*-butyl (2)	0.346 0.337	0.344 0.337	0.003 0.000	99.4 100.0
Butyraldehyde (1) di-*n*-butyl (2)	0.346 0.346	0.333 0.324	0.000 †	96.2 93.6
Benzaldehyde (1) diallyl (2)	0.316 0.346	0.277 0.309	† 0.001	87.7 89.3
Butyraldehyde (1) diallyl (2)	0.136 0.136	0.109 0.109	0.003 †	80.2 80.2

**The abundances shown are the excess above the value 0.206% found for normal benzaldehyde di-n-butyl acetal when it was compared with Lake Ontario water to which a value of 0.204% had been assigned (15).*

†*Not determined.*

excess O^{18} originally present in the aldehyde reappeared in the water of condensation. This result and the trend of the values shown in the last column of the table can be readily understood on the assumption that, in competition with acetal formation, there is a reaction of the alcohol producing an ordinary ether and water of normal O^{18} abundance. Of the two alcohols, allyl and butyl, the former reacts more slowly in the acetal reaction (14), but is very much more reactive in simple ether formation. Furthermore, of the two aldehydes entering into the acetal reaction, benzaldehyde is the more reactive (1). Greatest dilution with normal water would, therefore, be expected in the *n*-butyraldehyde – allyl alcohol system, and least dilution in the reaction of benzaldehyde with *n*-butyl alcohol. This has been found to be the case.

The results of the acetal hydrolysis studies are shown in Table II. With the exception of the reaction of the acetal derived from allyl alcohol, the alcohol product contained, within experimental error, the normal abundances of the oxygen isotopes. Allyl alcohol was slightly enriched, a result to be ex-

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pected since this alcohol has been shown to slowly exchange its oxygen with water under the conditions of the experiment. (See Experimental section.)

TABLE II

OXYGEN-18 RESULTS FOR ACETAL HYDROLYSIS

Acetal		Isotope abundances (atom % excess)*	
		Water	Alcohol product
Benzaldehyde di-*n*-butyl		0.371	−0.001
Butyraldehyde di-*n*-butyl		0.371	−0.003
Benzaldehyde diallyl	(1)	0.444	+0.033
	(2)	0.522	+0.016

**See first footnote to Table I.*

These results quite definitely establish that it is the bond of oxygen to the aldehyde carbon which undergoes fission in the reversible reaction of acetal formation and hydrolysis. Two mechanisms are consistent with this finding, namely the carbonium ion mechanism proposed by Ingold and a bimolecular process involving attack of the reagent on the conjugate acid of the hemiacetal or acetal. The latter mechanism, however, would appear to have been eliminated as a possibility by the recent observation of McIntyre and Long (6, 8) that the rate of hydrolysis of methylal is a linear function of the Hammett acidity function, H_0, indicating that no water molecules are firmly bound in the transition state. It is of interest that the present work shows that the carbonium ion is derived from the aldehyde part of the molecule even in systems involving allyl alcohol in which a carbonium ion derived from the alcohol would be mesomeric.

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DEPOLARIZATION BY MERCAPTOACETIC ACID DURING ELECTRODEPOSITION OF COPPER[1]

By A. J. Sukava[2] and C. A. Winkler

ABSTRACT

Mercaptoacetic acid (MAA) in acid copper sulphate electrolyte decreased the cathode polarization throughout the course of electrolysis at all concentrations up to 20 mgm./liter. Addition of small amounts of chloride caused further depolarization. When present together with cystine, MAA showed an independence of action. The depolarization caused by MAA was ascribed to a decreased activation overpotential due to substitution of a more readily dischargeable MAA–copper complex for the aquo–copper complex. The additional depolarization due to chloride was ascribed to formation of a still more readily dischargeable chloro–MAA–copper complex. The depolarization in both cases increased with time during prolonged electrolysis, apparently due to surface roughening with, presumably, a consequent increase in surface area and decrease in true current density.

INTRODUCTION

Investigations have recently been made in this laboratory into the addition agent effects, during electrodeposition of copper, of some simple amino compounds (1, 5). These compounds are known to be positively charged in acid solution and to be capable of co-ordination with copper ions. In the course of these studies, it became of interest to inquire whether a sulphur-containing carboxylic acid lacking the amino group, and with no positive charge in the solution, would show any fundamental difference in behavior from that of the amino compounds studied. Preliminary experiments with mercaptoacetic acid (MAA) indicated an interesting behavior, more extended investigation of which gave the results reported in the present paper.

EXPERIMENTAL

The equipment and procedure were identical with those outlined previously (5). MAA was reagent grade. A stock solution of it in the standard electrolyte was made to a concentration of 0.05 gm./liter (the low solubility of a dark precipitate that formed limited the concentration to this value). This solution was diluted with standard electrolyte to give the desired concentration of MAA during electrolysis. All experiments were made at 24.5° C., with a current density of 2 amp./dm.^{2}.

RESULTS

MAA alone in the electrolyte reduced the total polarization below the 100-millivolt steady state value obtained with no additive (5). There was some indication of an indeterminate maximum in polarization during the initial 0.01 sec. (approximately), but the first distinct trace on the cathode ray oscilloscope showed a sharp drop in polarization and this depolarization by MAA continued throughout the electrolysis. The immediate effect of MAA

[1]*Manuscript received in original form July 28, 1955, and, as revised, November 14, 1955.*
Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Que., with financial assistance from the Consolidated Mining and Smelting Co., Trail, B.C., and the National Research Council of Canada, Ottawa, Canada.
[2]*Holder of a Cominco Research Fellowship. Present address: Department of Chemistry, University of Western Ontario, London, Ont.*

was to cause depolarization to about 50 to 60 mv. with a standard surface; the steady state polarization, established after electrolysis for an hour or more, was decreased to a limiting value of about 35 mv. as the concentration of MAA

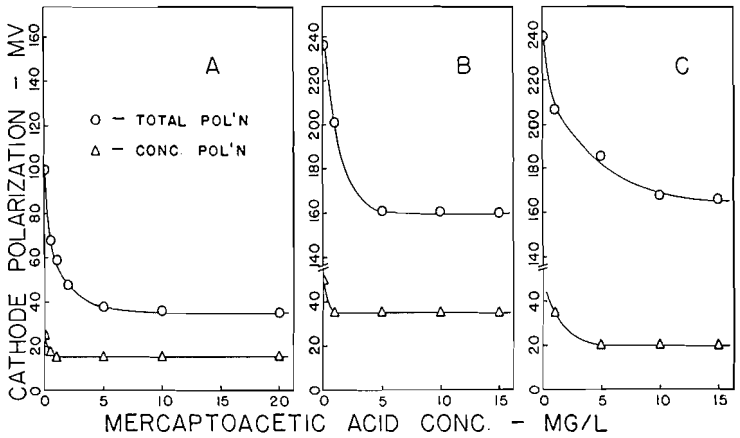

FIG. 1. Effect of mercaptoacetic acid concentration on steady state total and concentration polarizations.
A. Mercaptoacetic acid present alone.
B. Mercaptoacetic acid with 20 mgm./liter cystine.
C. Mercaptoacetic acid with 20 mgm./liter gelatin.

was increased, while the concentration polarization suffered a decrease of about 10 mv. (Fig. 1A). The steady state deposits obtained at these low polarizations had a characteristically coarse appearance under the microscope. These facts suggest that a gradual change in surface conditions, sufficient to decrease the true current density, is superimposed on the depolarizing action of the MAA. It seems reasonable to conclude that, in addition to the 15 mv. measured concentration polarization, there remains at the steady state about 20 mv. due to hydrogen ion interference (5).

The addition of chloride in low concentration caused further depolarization. Both the total and concentration polarizations at steady state, with 10 mgm./liter MAA, passed through a minimum at about 10 mgm./liter chloride ion (Fig. 2). The steady state polarization in the presence of chloride was also established slowly, just as in its absence. This greater depolarization due to chloride appeared to be accompanied by greater roughness of the cathode deposit. At the 20 mv. level of total polarization the crystal outgrowths were about 80 microns long. It should be noted, perhaps, that the concentration polarization at higher chloride concentrations increased to a limiting value of about 20 mv.

Since the polarization was decreased by MAA but increased by cystine (5) or gelatin (2), it was of interest to study the behavior when both depolarizing and polarizing addition agents were present. When various amounts of MAA were added with a fixed amount (20 mgm./liter) of cystine, the steady state polarization was lowered to a limiting value, the magnitude of the decrease being of the same order as that observed in the absence of cystine (Fig. 1B). Moreover, about 5 mgm./liter MAA gave maximum depolarization in either

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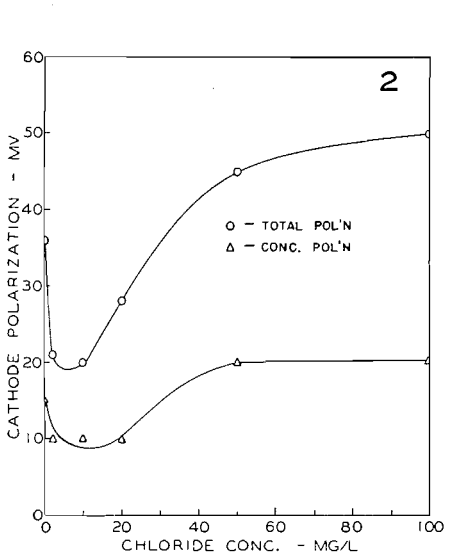
case. The 75 mv. decrease in polarization caused by MAA in the presence of cystine includes a 15 mv. decrease in concentration polarization; the difference, 60 mv., is to be compared with the corresponding difference of 55 mv. obtained with MAA alone.



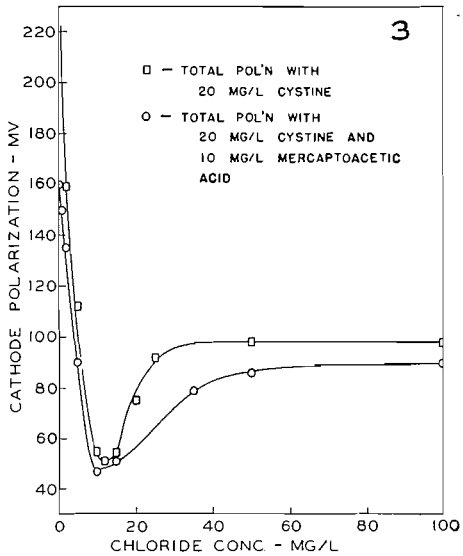


FIG. 2. Cathode polarization – chloride concentration relation in the presence of 10 mgm./liter mercaptoacetic acid.

FIG. 3. Cathode polarization – chloride concentration relation with 20 mgm./liter cystine and with 20 mgm./liter cystine and 10 mgm./liter mercaptoacetic acid.

Study of the polarization–time relations when both MAA and cystine were present showed that during the first few seconds of electrolysis the total polarization values were as low as 60 mv. A rapid increase to a maximum after one or two minutes was followed by approach to a steady state during the next two to three hours. The steady state deposits, when both addition agents were present, were smooth and had none of the gray tinge imparted to the deposit by cystine alone. The following data were obtained with 20 mgm./liter cystine and different concentrations of MAA:

Time	Total polarization (mv.) Mercaptoacetic acid concentration (mgm./liter)			
	1	5	10	15
0	(Initial maxima not measurable)			
2 sec.	80	85	73	60
¼ min.	155	132	113	93
½ min.	188	158	125	107
1 min.	203	170	142	110
2 min.	207	173	140	108
10 min.	209	183	150	114
20 min.	211	182	153	120
30 min.	209	179	153	123
40 min.	208	176	154	130
110 min.	201	166	152	149
120 min.	202	167	153	150
290 min.	202	161	159	159
330 min.	201	161	161	160

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As indicated, the higher concentrations of MAA accentuated the depolarization during the early stages of electrolysis, though not at the steady state.

Addition of small concentrations of chloride practically eliminated the influence of MAA in the presence of cystine (Fig. 3). It should be noted, however, that with excess chloride the total steady state polarization in the presence of MAA was about 15 mv. lower than in its absence. Also, the levelling-off of the total polarization curve required a greater amount of chloride when MAA was added to the electrolyte. The presence of MAA with excess chloride and 20 mgm./liter cystine did not affect the concentration polarization, which was about 20 to 25 mv. The polarization–time curves with chloride present were essentially the same as those obtained with the same amount of cystine in the absence of MAA (5).

Experiments with a combination of 20 mgm./liter gelatin and different amounts of MAA showed an effect on the steady state polarization similar to that observed with cystine (Fig. 1C). Addition of chloride to such a system gave a polarization – chloride concentration relation similar in its essential features to that obtained with gelatin and chloride in the absence of MAA (4). The polarization–time relations were rather complex. They resembled those obtained with small concentrations of thiourea (5) in the respect that the polarization increased rather sharply after about one hour's electrolysis, after which it either increased further, or decreased slowly to the steady state value, depending on the concentration of chloride.

DISCUSSION

The immediate depolarizing effect of MAA, shown by initial polarization values, indicates that the activation overpotential was reduced to but a few millivolts. Accompanying the rough surface laid down, a further decrease in activation overpotential, hydrogen ion interference, and concentration polarization gradually occurred, probably because of decrease in true current density with an increase of true cathode area.

The behavior of MAA is in striking contrast with that of cystine, which appeared to leave the activation overpotential unaltered, but to increase the total polarization by adsorption on the cathode (5). If reference is made to the views of Lyons (3) the difference in behavior might be ascribed to a higher activity of cystine and a lower activity of MAA, relative to that of water, at the cathode surface. This might be expected since positively charged cystine, but not the neutral MAA, should tend to accumulate at the cathode surface. According to this point of view, such differences in activity of the co-ordinating species may be reflected in the relative activation overpotentials involved.

The observed additivity of the cystine and MAA effects at steady state gives clear indication that the two substances act in large measure independently. If, as argued previously (5), the aquo–copper complex is discharged in the presence of cystine, the reduction in activation overpotential with MAA is probably due to the ready discharge of the MAA–copper complex.

Although MAA should not accumulate at the cathode as a result of electrostatic attraction, it might well be readily adsorbed. Indeed, the behavior of MAA in the presence of cystine during the early stages of electrolysis suggests

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that preferential adsorption of the MAA probably does occur prior to electrolysis. This could account for the observation that the depolarizing effect with higher concentrations of MAA is greater during the early stages than at steady state. However, the hindrance to the adsorption of cystine by such adsorbed MAA could be slowly overcome by gradual accumulation of cystine at the cathode surface. If MAA in the adsorbed phase were present as a readily dischargeable MAA–copper complex, it would not contribute to increase in polarization.

The additional depolarization caused by chloride in the presence of MAA apparently arises from increased roughening of the surface when chloride is present. This might be due to discharge of a more readily dischargeable chloro–MAA–copper complex, the presence of which is assumed, rather than the MAA–copper complex. Support for this assumption may be found in a previous argument (5) that chloride, when present alone, does not affect the activation overpotential. Hence, it does not appear that the depolarizing effect of chloride in the presence of MAA could be due to any readily dischargeable chloro–copper or chloro–aquo–copper complexes. For chloride concentrations above that corresponding to the minimum in the polarization – chloride concentration curve (Fig. 2), adsorption of cuprous chloride (5) might be expected to decrease the active surface area of the cathode, hence increase the true current density. This, in turn, might be expected to increase the difference between total and concentration polarization and this is observed. The 20-mv. plateau in the concentration–polarization curve (Fig. 2) might be regarded as a maximum diffusion and convection effect with increasing true current density.

Since the effect of low concentrations of chloride in the presence of both cystine and MAA more closely resembles its effect with cystine alone than with MAA alone (Fig. 3), the chloride effect is preferential in favor of cystine. For chloride concentrations above the minimum polarization point, more chloride appears to be necessary to produce the limiting maximum polarization (due to cuprous chloride (5)), when MAA is present with cystine than when cystine is present alone. Moreover, the effect of MAA in this combination is to lower the limiting maximum, which indicates a decrease in activation overpotential alone since the concentration polarization, hydrogen ion interference, and adsorption polarization due to cuprous chloride would be essentially the same in the two cases. These effects are to be expected if some of the chloride not tied up in the chloro–cystine–copper complex (5) associates with the MAA, possibly as the readily dischargeable chloro–MAA–copper complex.

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THE CRYSTAL STRUCTURES OF SOME INTERMETALLIC COMPOUNDS OF PLUTONIUM[1]

By O. J. C. Runnalls

ABSTRACT

The crystal structures of the following binary intermetallic compounds of plutonium are reported: $PuAl_2$, $PuAl_3$, $PuAl_4$, $PuBe_{13}$, $PuCo_2$, $PuFe_2$, $PuMn_2$, $PuNi_2$, $PuNi_5$, and Pu_2Ni_{17}. In addition, the unit cell dimensions are reported for $PuAg_3$.

INTRODUCTION

It is now possible to report on the crystal structures of intermetallic compounds of plutonium, because of a recent declassification decision. X-ray data have been compiled in this paper for 11 such compounds. The present data are compared with American (5) and Russian (9) data released recently, in Appendix I at the end of the paper.

All X-ray powder photographs were taken on a 14.3 cm. diameter General Electric camera, using Ni-filtered Cu radiation. The single crystal photographs were taken on a G.E. rotation camera of 5 cm. radius. The wave-lengths used in the calculations were 1.5418 Å for Cu K_α and 1.5405 for Cu K_{α_1}.

EXPERIMENTAL

1. *Plutonium–Aluminum Alloys*

Plutonium–aluminum alloys were prepared in BeO crucibles by the reduction of 99.5% pure plutonium trifluoride with 99.99% pure aluminum in vacuum at 900° C. Three intermediate Pu–Al phases have been identified using X-ray diffraction analyses—$PuAl_2$, $PuAl_3$, and $PuAl_4$.

(*a*) *$PuAl_2$*

A powder diffraction pattern showed that $PuAl_2$ is face-centered cubic with $a_0 = 7.831 \pm 0.005$ Å. The compound is isostructural with UAl_2 (11) and, therefore, has the $MgCu_2$ structure. The face-centered positions in space group $Fd3m$ are

$$8 \text{ Pu in } 0, 0, 0; \tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{4}$$

$$16 \text{ Al in } \tfrac{5}{8}, \tfrac{5}{8}, \tfrac{5}{8}; \tfrac{5}{8}, \tfrac{3}{8}, \tfrac{3}{8}; \tfrac{3}{8}, \tfrac{5}{8}, \tfrac{3}{8}; \tfrac{3}{8}, \tfrac{3}{8}, \tfrac{5}{8}.$$

The calculated density is 8.10 gm. cm.$^{-3}$, assuming eight $PuAl_2$ molecules per unit cell. The interatomic distances are tabulated in Table I.

(*b*) *$PuAl_3$*

The powder diffraction pattern for $PuAl_3$ proved more complex than the simple cubic UAl_3, where $a_0 = 4.287$ Å (11). However, approximately one-third of the diffraction lines could be indexed on a simple cubic pattern of $a_0 = 4.30$ Å. Hence, it seemed probable that the $PuAl_3$ configuration was the result of a minor shift in the UAl_3-type cubic close-packing.

[1]*Manuscript received September 8, 1955.*
Contribution from the Chemistry and Metallurgy Division, Atomic Energy of Canada Limited, Chalk River, Ontario. Issued as A.E.C.L. No. 267.

Single crystals of $PuAl_3$ were separated from a 40 wt. % Pu–Al alloy after dissolving the aluminum matrix in 3 *N* NaOH. Several of the hexagonal-

TABLE I

INTERATOMIC DISTANCES IN $PuAl_2$

Atom	Neighbor	Number of neighbors	Distance, Å
Pu	Pu	4	3.39
	Al	12	3.25
Al	Pu	6	3.25
	Al	6	2.77

shaped crystals illustrated in Fig. 2 proved suitable as single crystal X-ray specimens. A series of rotation photographs revealed that the primitive cell was hexagonal with lattice dimensions

$$a_0 = 6.08 \pm 0.01 \text{ Å}$$

$$c_0 = 14.40 \pm 0.03 \text{ Å}.$$

The calculated density is 6.92 gm. cm.$^{-3}$, assuming six molecules per unit cell. A Laue photograph of a $PuAl_3$ crystal exhibited dihexagonal symmetry, identifying the point group as 622, $6mm$, $\bar{6}m2$, or $6/mmm$.

A model for the unit cell consistent with the observed dimensions was constructed using six close-packed planes, each containing one $PuAl_3$ molecule (Fig. 1). The model is derived by stacking the first four layers in cubic close-packed positions similar to UAl_3, and inserting a mirror plane at $c = \frac{1}{2}$, i.e.

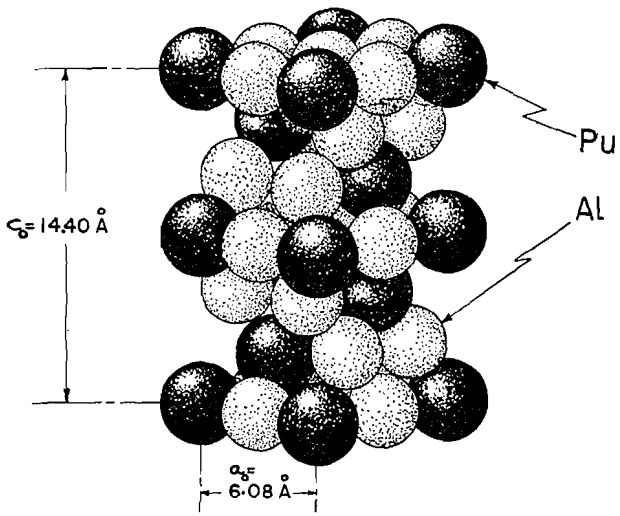

FIG. 1. An approximate model of the $PuAl_3$ unit cell.

[ABCACB]ABCAC—. This configuration is described in the International Tables (7) by the space group $P\bar{6}m2$, or, as pointed out by the Los Alamos

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group (8), $P6_3/mmc$. Calculated intensities are reported in Table II for the following atomic positions in $P\bar{6}m2$:*

1 Pu in (a) 0, 0, 0
1 Pu in (b) 0, 0, $\frac{1}{2}$
2 Pu in (h) $\frac{1}{3}, \frac{2}{3}, z; \frac{1}{3}, \frac{2}{3}, \bar{z}; z = \frac{1}{6}$
2 Pu in (i) $\frac{2}{3}, \frac{1}{3}, z; \frac{2}{3}, \frac{1}{3}, \bar{z}; z = \frac{1}{3}$
3 Al in (j) $x, \bar{x}, 0; x, 2x, 0; 2\bar{x}, \bar{x}, 0; x = -\frac{1}{2}$
3 Al in (k) $x, \bar{x}, \frac{1}{2}; x, 2x, \frac{1}{2}; 2\bar{x}, \bar{x}, \frac{1}{2}; x = -\frac{1}{2}$
6 Al in (n) $x, \bar{x}, z; x, 2x, z; 2\bar{x}, \bar{x}, z; x, \bar{x}, \bar{z}; x, 2x, \bar{z}; 2\bar{x}, \bar{x}, \bar{z}; x = -\frac{1}{6}, z = \frac{1}{6}$
6 Al in (n) $x = \frac{1}{6}, z = \frac{1}{3}$.

TABLE II

POWDER DIFFRACTION DATA FOR $PuAl_3$

$hk.l$	$\sin^2\theta$		I	
	Calc.	Obs.	Obs.*	Calc.†
10.1	0.0243	0.0250	w	2.4
00.3	0.0258	—	abs.	0
10.2	0.0329	0.0337	s	5.0
00.4	0.0459	—	abs.	0
10.3	0.0472	0.0478	s	4.4
11.0	0.0643	0.0652	s	4.5
11.1	0.0672	0.0681	m	0
10.4	0.0673			2.1
00.5	0.0717	—	abs.	0
11.2	0.0758	—	abs.	0
20.0	0.0857	—	abs.	0
20.1	0.0886	0.0896	w	1.2
11.3	0.0901	—	abs.	0
10.5	0.0931	0.0947	vw	0.5
20.2	0.0972	0.0981	s	3.0
00.6	0.1032	0.1037	m	1.9
20.3	0.1115	0.1121	s	3.4
10.6	0.1246	—	abs.	0
20.4	0.1316	0.1318	m	2.0
11.5	0.1360	—	abs.	0
00.7	0.1404	—	abs.	0
12.0	0.1501	—	abs.	0
12.1	0.1529	0.1540	vw	0.5
20.5	0.1574	0.1582	vw	0.5
12.2	0.1615	0.1625	m	1.3
10.7	0.1619			0.2
11.6	0.1675	0.1679	m+	2.4
12.3	0.1758	0.1760	m	1.6
00.8	0.1834	—	abs.	0
20.6	0.1889	—	abs.	0
30.0	0.1929	0.1933	m−	1.0
30.1	0.1958	0.1957	m−	0
12.4	0.1959			1.0
30.2	0.2044	0.2046	w−	0.5
10.8	0.2049			0
30.3	0.2187	—	abs.	0
12.5	0.2217	0.2220	w−	0.3
20.7	0.2262	0.2268	w−	0.3
00.9	0.2321	—	abs.	0
30.4	0.2384	—	abs.	0
22.0	0.2572	0.2583	m	1.4
13.0	0.2786	—	abs.	0

*s = *strong*, m = *medium*, w = *weak*, vw = *very weak*, and *abs.* = *absent*.

†$I \propto |F|^2 p[(1+\cos^2 2\theta)/\sin^2\theta \cos\theta]$.

**The equivalent positions in $P6_3/mmc$ are 2 Pu in (b), 4 Pu in (f) with $z = 1/12$, 6 Al in (h) with $x = \frac{1}{2}$, and 12 Al in (k) with $x = \frac{1}{6}$ and $z = 7/12$.*

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The intensities of neighboring reflections only were compared, since no absorption correction was used in the calculations. Since the calculated intensities agreed with those observed on the powder diffraction film, the unit cell model appeared a reasonable one (see Table II).

The above solution may be considered only an approximate one, however, since weak reflections have been observed for 00.4, 00.8, 00.10, 00.14, and 00.16 by the Los Alamos group on Weissenberg patterns (8). Stambaugh found that the interplanar distances in the [00.1] direction were $0.162 \pm 0.002\ c_0$ for AB and CA, and $0.176 \pm 0.004\ c_0$ for BC, instead of the equiplanar distance of $0.167\ c_0$ (5). Unfortunately, this solution is not considered unique since satisfactory intensity checks for all *hk.l* values were not completed (5).

If all the Pu atoms were equidistant in the $PuAl_3$ cell the expected length of the c_0 axis would be 14.88 Å, instead of the observed 14.40 Å, to conform with the observed Pu–Pu separation in the [10.0] direction. Stambaugh's results indicate that the 0.48 Å shrinkage in c_0 is confined to those planes which do not have the UAl_3-type stacking sequence; i.e. if the shrinkage was distributed equally over the planes BAB and CAC the interplanar distances in the [00.1] direction would be $0.164\ c_0$ for AB and CA, and $0.172\ c_0$ for BC.

(*c*) *$PuAl_4$*

A 20 wt. % Pu–Al alloy was reacted with 3 *N* NaOH to dissolve the aluminum matrix. The powder diffraction pattern of the crystalline residue was complex, and similar to the UAl_4 pattern. Single crystals of $PuAl_4$ were prepared by cooling a molten 20% Pu–Al alloy at 100° C. per hr., and dissolving away the excess aluminum in NaOH. One of the small needlelike crystals (Fig. 3) was mounted in a quartz capillary.

A series of rotation photographs showed that $PuAl_4$ has an orthorhombic unit cell with dimensions similar to UAl_4 (see Table III). The calculated density is 6.10 gm. cm.$^{-3}$, assuming four molecules per unit cell. The spectra found missing by Borie (3) in the UAl_4 analysis were missing in the $PuAl_4$ pattern also; i.e. the reflections present were

(*a*) $h\ k\ l$, only for $h+k+l = 2n$
(*b*) $h\ k\ 0$, only for $h = 2n$ and $k = 2n$
(*c*) $h\ 0\ l$, only for $h+l = 2n$
(*d*) $0\ k\ l$, only for $k+l = 2n$.

TABLE III
UNIT CELL DIMENSIONS FOR $PuAl_4$ and UAl_4

	$PuAl_4$, Å	UAl_4 (3), Å
a_0	4.42 ± 0.02	4.41 ± 0.02
b_0	6.26 ± 0.02	6.27 ± 0.02
c_0	13.66 ± 0.03	13.71 ± 0.03

These data indicate that the cell is body-centered with an 00*l* glide plane and may be described by either the space group *Ima*2 or *Imma*.

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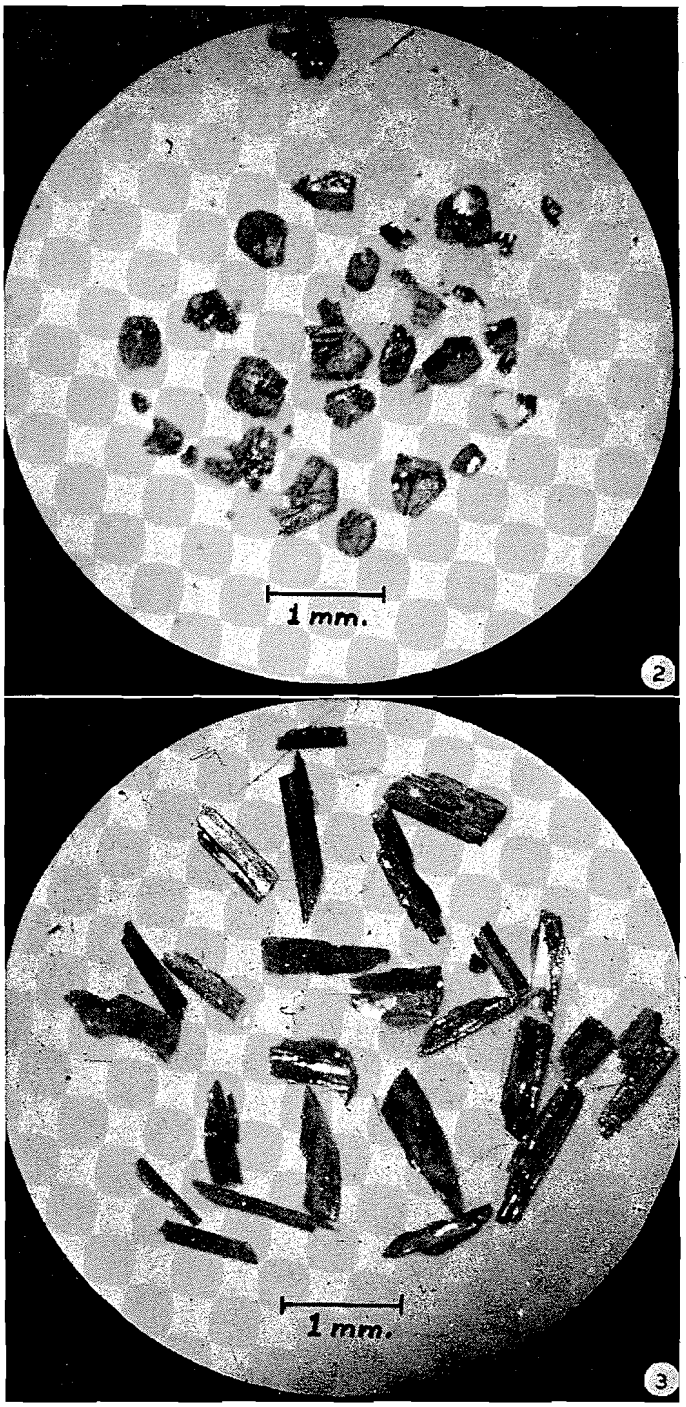

Fig. 2. Single crystals of $PuAl_3$.
Fig. 3. Single crystals of $PuAl_4$.

A visual comparison of the intensities on the $PuAl_4$ and UAl_4 powder patterns showed the two to be identical. Hence, Borie's description for UAl_4 (3) is applicable to $PuAl_4$ using atomic positions in space group *Imma*.

$(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2})+$
4 Pu in (e) $0, \frac{1}{4}, z; 0, \frac{3}{4}, \bar{z}; z = 0.111$
4 Al in (e) $0, \frac{1}{4}, z; 0, \frac{3}{4}, \bar{z}; z = -0.111$
4 Al in (b) $0, 0, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}$
8 Al in (h) $0, y, z; 0, \bar{y}, \bar{z}; 0, \frac{1}{2}+y, \bar{z}; 0, \frac{1}{2}-y, z; y = -0.033, z = 0.314.$

Singer has concluded that the value $z = 0.113$ for the 4 Pu atoms in (e) gives better intensity agreement than $z = 0.111$ (5). The interatomic distances are listed in Table IV.

TABLE IV
INTERATOMIC DISTANCES IN $PuAl_4$

Atom	Neighbor	Number of neighbors	Distance, Å
Pu(4*e*)	Al(4*e*)	2	3.13
	Al(4*e*)	1	3.03
	Al(4*b*)	4	3.11
	Al(8*h*)	4	3.01
	Al(8*h*)	2	3.29
Al(4*e*)	Pu(4*e*)	2	3.13
	Pu(4*e*)	1	3.03
	Al(4*b*)	4	3.11
	Al(8*h*)	4	2.79
	Al(8*h*)	2	3.09
Al(4*b*)	Pu(4*e*)	4	3.11
	Al(4*e*)	4	3.11
	Al(4*b*)	2	3.13
	Al(8*h*)	2	2.55
Al(8*h*)	Pu(4*e*)	2	3.01
	Pu(4*e*)	1	3.29
	Al(4*e*)	2	2.79
	Al(4*e*)	1	3.09
	Al(4*b*)	1	2.55
	Al(8*h*)	2	2.82
	Al(8*h*)	1	3.54
	Al(8*h*)	1	2.72

2. *Plutonium–Beryllium Alloys*

Plutonium–beryllium alloys were prepared in BeO crucibles by the reduction of plutonium trifluoride with powdered beryllium metal, 99.8% pure, in vacuum at 1100–1200° C. At these temperatures the beryllium fluoride product readily distilled, leaving a fluoride-free alloy.

The powder diffraction pattern of the intermediate phase $PuBe_{13}$ was readily interpreted since the compound is face-centered cubic and is isostructural with UBe_{13}. The lattice constant, a_0, decreases from 10.284 ± 0.001 Å on the Be-rich side to 10.278 ± 0.001 Å on the Pu-rich side, indicating some

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small range of solid solubility. The calculated density, assuming eight formula weights of $PuBe_{13}$, is 4.35 gm. cm.$^{-3}$.

The compound UBe_{13} has been found isostructural with $NaZn_{13}$ and is described by the space group *Fm3c* (1). The $NaZn_{13}$ parameters reported by Zintl and Hauche (15) have been refined recently by Shoemaker *et al.* (14). These refined parameters, $y = 0.1806$ and $z = 0.1192$, were used in calculating the interatomic distances in the $PuBe_{13}$ cell (Table V).

TABLE V

INTERATOMIC DISTANCES IN $PuBe_{13}$

Atom	Neighbor	Number of neighbors	Distance, Å
$Be_I(0, 0, 0)$	$Be_{II}(0, y, z)$	12	2.22
Be_{II}	$Be_{II}(0, z, \frac{1}{2}-y)$	2	2.15
	$Be_I(0, 0, 0)$	1	2.22
	$Be_{II}(z, \frac{1}{2}-y, 0)$	2	2.25
	$Be_{II}(z, 0, y)$	4	2.31
	$Be_{II}(0, y, \bar{z})$	1	2.45
	$Pu(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$	2	2.99
$Pu(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$	$Be_{II}(0, y, z)$	24	2.99

The observed contraction of $PuBe_{13}$ on the Pu-rich side is somewhat surprising, since the Pu atom is about 35% larger than the Be atom. The isostructural $NpBe_{13}$ lattice also contracts, on the Np-rich side (12). A similar phenomenon has been observed by Bradley and Taylor (4) for the Al-rich side of the phase NiAl; i.e. the lattice spacing decreases rapidly with an increasing aluminum ratio. The latter effect has been attributed to the generation of nickel vacancies in the lattice as the aluminum ratio increases. A similar defect structure, Be-deficient, may exist in Pu-rich $PuBe_{13}$.

3. *Plutonium – Transition Metal Alloys*

Alloys of plutonium with the transition elements manganese, iron, cobalt, and nickel have been prepared by heating an intimate mixture of plutonium trifluoride and transition metal powder, 99.99% pure, in the presence of lithium vapor at 950° C. The product was then heated at 1100° C. for 15 min. Satisfactory Pu–Fe and Pu–Ni alloys were prepared in BeO crucibles. The best Pu–Co and Pu–Mn alloys, however, were prepared in Ta containers, since the latter alloys soaked into BeO.

(*a*) *PuX_2-type Phases*

X-ray powder photographs of alloys containing 65–70 wt. % Pu showed a face-centered cubic phase, isostructural with UFe_2 (2). Two separate preparations of $PuFe_2$ showed different lattice constants, indicating a range of composition for this phase. The observed lattice dimensions and calculated densities for the PuX_2 compounds are listed in Table VI. All four compounds have the $MgCu_2$ structure in space group *Fd3m*, with eight formula weights per unit cell. Interatomic distances are shown in Table VII.

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TABLE VI

UNIT CELL SIZE AND X-RAY DENSITY FOR PuX_2-TYPE PHASES

Compound	Lattice dimension, Å	Calculated density, gm. cm.$^{-3}$
$PuMn_2$	7.290±0.005	11.96
$PuFe_2$	(*a*) 7.150±0.005	12.74
	(*b*) 7.190±0.005	12.53
$PuCo_2$	7.075±0.005	13.39
$PuNi_2$	7.16 ±0.01	12.90

TABLE VII

INTERATOMIC DISTANCES IN THE COMPOUNDS PuX_2 WHERE X = Mn, Fe, Co, or Ni

			Distance, Å				
				$PuFe_2$			
Atom	Neighbor	Number of neighbors	$PuMn_2$	(*a*)	(*b*)	$PuCo_2$	$PuNi_2$
Pu	Pu	4	3.16	3.10	3.12	3.06	3.10
	X	12	3.02	2.96	2.98	2.93	2.96
X	X	6	2.58	2.53	2.54	2.50	2.53
	Pu	6	3.02	2.96	2.98	2.93	2.96

(*b*) *$PuNi_5$*

A powder photograph of a Pu–Ni alloy near the composition $PuNi_5$, 45 wt. % Pu, showed a single phase which was indexed on a hexagonal lattice with dimensions

$$a_0 = 4.875 \pm 0.005 \text{ Å},$$

$$c_0 = 3.970 \pm 0.005 \text{ Å}.$$

The X-ray data resembled closely those for the compound $ThNi_5$, which has the $CaZn_5$ structure (6). Calculated intensities based on this structure are in reasonable agreement with the observed powder data for $PuNi_5$, as shown in Table VIII.

Thus, $PuNi_5$ may be described by the $CaZn_5$ structure with the following atomic positions in space group $P6/mmm$:

1 Pu in 0, 0, 0

2 Ni_I in $\frac{1}{3}, \frac{2}{3}, 0; \frac{2}{3}, \frac{1}{3}, 0$

3 Ni_{II} in $\frac{1}{2}, 0, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.

The calculated density is 10.82 gm. cm.$^{-3}$.

Interatomic distances are listed in Table IX.

(*c*) *Pu_2Ni_{17}*

Since $PuNi_5$ proved to be isostructural with $ThNi_5$, a search was made for a Pu–Ni compound isomorphous with Th_2Ni_{17}. A phase with an X-ray pattern

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TABLE VIII

POWDER DIFFRACTION DATA FOR $PuNi_5$

hk.l	$\sin^2\theta$		*I*	
	Calc.	Obs.	Obs.†	Calc.‡
10.0	0.0333	0.0348	m−	246
10.1	0.0710	0.0731	s	1109
11.0	0.1000	0.1029	m	547
20.0	0.1307	0.1365	m	536
11.1	0.1377	0.1408	s+	1400
00.2	0.1508	0.1523	m−	341
20.1	0.1711	—	abs.	0
10.2	0.1841	0.1881	w−	70
21.0	0.2317	0.2381	w−	51
11.2	0.2509	0.2538	m	275
21.1	0.2711	0.2743	m	312
20.2	0.2842	0.2870	m+	320
30.0	0.3001	0.3031	w+	102
30.1	0.3378	0.3415	m	321
00.3	0.3394	—	abs.	10
10.3	0.3727	0.3736	w+	94
21.2	0.3842	0.3860	w	49
22.0	0.4001	0.4039	m	201
31.0	0.4334	0.4345	vw	21
22.1	0.4378	0.4408	s−	43
11.3	0.4394			216
30.2	0.4509	0.4525	w+	109
31.1	0.4711	0.4735	m−	135
20.3	0.4727			0.2
40.0	0.5213	0.5284	vw	64
22.2	0.5509	0.5532	m	272
40.1	0.5712	0.5748	m	0.1
21.3	0.5727			111
31.2	0.5843	0.5878	vw	30
00.4	0.6028	0.6048	vw	43
32.0	0.6335	—	abs.	15
10.4	0.6367	0.6405	m+	15
30.3	0.6383			157
32.1	0.6712	0.6746	w	110
40.2	0.6843	0.6875	w	119
41.0	0.7001	0.7038	m	85
11.4	0.7033			85
20.4	0.7354			125
41.1	0.7359	0.7388	s	335
22.3	0.7375			34
31.3	0.7715	0.7740*	w	123
32.2	0.7830	0.7852*	vw	36
50.0	0.8321	—	abs.	10
21.4	0.8353	0.8360*	vw	40
41.2	0.8495	0.8513*	m	227
50.1	0.8697	0.8725*	w−	81
40.3	0.8713	—	abs.	0.6
33.0	0.8987	0.8993*	w−	71
30.4	0.9019	0.9026*	w	142
42.0	0.9319	0.9337*	m−	242
33.1	0.9363	0.9374*	m+	334
00.5	0.9411	—	abs.	14
42.1	0.9696	—	abs.	4
32.3	0.9712	0.9714*	m+	354
10.5	0.9744	0.9740*	w	186
50.2	0.9827	0.9826*	vw	69

*$Cu\ K_{\alpha_1}$ *reflection.*

†*s = strong, m = medium, w = weak, vw = very weak, abs. = absent.*

‡$I \propto |F|^2 p[(1+\cos^2 2\theta)/\sin^2\theta\cos\theta]$.

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TABLE IX

INTERATOMIC DISTANCES IN $PuNi_5$

Atom	Neighbor	Number of neighbors	Distance, Å
Pu	Ni_I	6	2.82
	Ni_{II}	12	3.14
Ni_I	Pu	3	2.82
	Ni_I	3	2.82
	Ni_{II}	6	2.44
Ni_{II}	Pu	4	3.14
	Ni_I	4	2.44
	Ni_{II}	4	2.44

similar to, but more complex than, $PuNi_5$ was observed in alloys containing 30–35 wt. % Pu. This pattern was solved using a hexagonal lattice of dimensions

$$a_0 = 8.30 \pm 0.01 \text{ Å},$$

$$c_0 = 8.00 \pm 0.01 \text{ Å}.$$

The isomorphous phase Th_2Ni_{17} has $a_0 = 8.37$ Å and $c_0 = 8.14$ Å (6). Since the intensities in the powder patterns of Th_2Ni_{17} and Pu_2Ni_{17} are closely related it seems reasonable to assign the Th_2Ni_{17} structure to Pu_2Ni_{17}. The following approximate atomic positions apply in space group $P6_3/mmc$, for two molecules per unit cell:
2 Pu_I in (b), 2 Pu_{II} in (d), 6 Ni_I in (g), 12 Ni_{II} in (j) with $x = \frac{1}{3}$ and $y = 0$, 12 Ni_{III} in (k) with $x = \frac{1}{6}$ and $z = 0$, and 4 Ni_{IV} in (f) with $z = 0.11$.

4. *Plutonium–Silver Alloys*

Plutonium–silver alloys were prepared by heating in vacuum metallic Pu and fine-grain Ag of 99.97% purity in Ta crucibles at 1050° C. The Pu metal was prepared in 300 to 1000 mgm. amounts by the reduction of 99.5% pure PuF_3 with Li vapor at 950° C. During the alloying step the LiF slag covering the Pu metal distilled to the glass bulb surrounding the furnace assembly, leaving a clean alloy surface.

Powder diffraction patterns of Ag-rich alloys showed that a single phase existed at 40–45 wt. % Pu, i.e. $PuAg_3$. No attempt was made to apply graphical solution methods to the complex pattern since large hexagonal, columnar crystals could be separated from alloys approximating the composition $PuAg_3$. These proved satisfactory as single crystal X-ray specimens.

A series of rotation photographs showed that the $PuAg_3$ unit cell was hexagonal. Measurement of the layer line spacings gave lattice dimensions of

$$a_0 = 12.72 \pm 0.05 \text{ Å},$$

$$c_0 = 9.39 \pm 0.03 \text{ Å}.$$

These dimensions were refined by indexing the diffraction spots in the back reflection region of the zero layer lines. The diffraction angle, θ, was measured with a steel scale on a film which had been mounted in the camera according to the method of Straumanis. The pertinent X-ray data from a rotation about

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the c_0 axis are given in Table X. The crystal was adjusted for a rotation about the a_0 axis so that all but the 00.l planes were tilted away from the vertical. The Cu K_{α_1} diffraction spot from 00.12 was indexed and θ measured on the resulting photograph. The measured d-spacing was 0.7835 Å. The refined unit cell dimensions are

$$a_0 = 12.730 \pm 0.003 \text{ Å},$$

$$c_0 = 9.402 \pm 0.005 \text{ Å}.$$

TABLE X

X-RAY DATA FROM A ROTATION PHOTOGRAPH OF $PuAg_3$ ABOUT THE c_0 AXIS

$hk.l$	$d_{obs.}$, Å*	a_0, Å
87.0, 13.0.0	0.8479	12.728
96.0	0.8431	12.730
12.2.0	0.8405	12.728
10.5.0	0.8333	12.729
13.1.0	0.8148	12.727
12.3.0	0.8017	12.727
88.0	0.7955	12.728
97.0	0.7934	12.728
14.0.0, 10.6.0	0.7874	12.729
11.5.0	0.7776	12.730

**Obtained with Cu K_{α_1} radiation.*

The density of 450 mgm. of selected $PuAg_3$ crystals was measured with a pycnometer using ethylene dibromide as the immersion fluid. The resultant density was

$$\rho_{measured} = 11.16 \text{ gm. cm.}^{-3}.$$

If it is assumed that the unit cell contains 16 formula weights of $PuAg_3$, the density calculated from the X-ray data agrees closely with the measured value, i.e.

$$\rho_{calculated} = 11.33 \text{ gm. cm.}^{-3}.$$

The only systematic extinctions observed were of the type 00.l where $l = 2n+1$, indicating that the possible space groups for $PuAg_3$ are $P6_3$, $P6_3/m$, and $P6_322$.

Since a structure-type suggesting a solution for the $PuAg_3$ structure was not found in the literature, no further attempt was made to establish the atom positions in the unit cell.

DISCUSSION

Many more data on the binary intermetallic phases of neptunium, plutonium, and americium are required before the alloying systematics of the transuranic elements are understood. Sufficient information is available, however, to indicate that the alloying properties of the actinides are not necessarily similar in a specific alloy environment. The element plutonium, for example, exhibits isomorphism with uranium in the compounds $PuAl_2$ and $PuAl_4$ but not in $PuAl_3$, and with thorium in $PuNi_5$ and Pu_2Ni_{17} but not in $PuNi_2$. Further marked

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APPENDIX I

X-RAY DATA FOR SOME BINARY INTERMETALLIC COMPOUNDS OF PLUTONIUM

Compound	Structure type	Crystal system	Lattice constants, Å	Formula weights per unit cell	Space group	American results (5), Å	Russian results (9), Å
$PuAl_2$	$MgCu_2$	F.C.C.*	$a_0 = 7.831 \pm 0.005$	8	$Fd3m$	Pu-rich: $a_0 = 7.838 \pm 0.001$ Al-rich: $a_0 = 7.848 \pm 0.001$	
$PuAl_3$	$PuAl_3$	Hexagonal	$a_0 = 6.08 \pm 0.01$ $c_0 = 14.40 \pm 0.03$	6	$P6_3/mmc$ (8)	$a_0 = 6.17 \pm 0.02$ $c_0 = 14.5 \pm 0.1$	
$PuAl_4$	UAl_4	Orthorhombic	$a_0 = 4.42 \pm 0.02$ $b_0 = 6.26 \pm 0.02$ $c_0 = 13.66 \pm 0.03$	4	$Ima2$ or $Imma$	$a_0 = 4.40$ $b_0 = 6.28$ $c_0 = 13.79$	
$PuBe_{13}$	$NaZn_{13}$	F.C.C.	Pu-rich: $a_0 = 10.278 \pm 0.001$ Be-rich: $a_0 = 10.284 \pm 0.001$	8	$Fm3c$	Be-rich: $a_0 = 10.282 \pm 0.001$	10.274 ± 0.002
$PuCo_2$	$MgCu_2$	F.C.C.	$a_0 = 7.075 \pm 0.005$	8	$Fd3m$	Pu-rich: $a_0 = 7.081 \pm 0.001$	
$PuFe_2$	$MgCu_2$	F.C.C.	(*a*) $a_0 = 7.150 \pm 0.005$ (*b*) $a_0 = 7.190 \pm 0.005$	8	$Fd3m$	Pu-rich: $a_0 = 7.191 \pm 0.001$	7.179
$PuMn_2$	$MgCu_2$	F.C.C.	$a_0 = 7.290 \pm 0.005$	8	$Fd3m$	Pu-rich: $a_0 = 7.292 \pm 0.001$	7.28
$PuNi_2$	$MgCu_2$	F.C.C.	$a_0 = 7.16 \pm 0.01$	8	$Fd3m$	Pu-rich: $a_0 = 7.141 \pm 0.001$ Ni-rich: $a_0 = 7.115 \pm 0.001$	7.14
$PuNi_5$	$CaZn_5$	Hexagonal	$a_0 = 4.875 \pm 0.005$ $c_0 = 3.970 \pm 0.005$	1	$P6/mmm$	Pu-rich: $a_0 = 4.872 \pm 0.002$ $c_0 = 3.980 \pm 0.001$ Ni-rich: $a_0 = 4.861 \pm 0.002$ $c_0 = 3.982 \pm 0.001$	
Pu_2Ni_{17}	Th_2Ni_{17}	Hexagonal	$a_0 = 8.30 \pm 0.01$ $c_0 = 8.00 \pm 0.01$	2	$P6_3/mmc$	$a_0 = 8.29 \pm 0.02$ $c_0 = 8.01 \pm 0.02$	
$PuAg_3$		Hexagonal	$a_0 = 12.730 \pm 0.003$ $c_0 = 9.402 \pm 0.005$	16	$P6_3$, $P6_3/m$, or $P6_322$		

*F.C.C. = *face-centered cubic.*

differences in alloying properties are illustrated by the absence of compounds of the type PuAl (5, 13) and AmAl (13), and Pu_3Al (5) in the systems U–Al and Np–Al.

Variable alloying characteristics in the early members of the actinide series might be expected, according to Mott (10), because of a variable valency resulting from an electron interchange between the 5*f* and 6*d* shells. Since existing evidence indicates that the binding energies for 5*f* and 6*d* electrons are nearly equal at neptunium, alloy data for neptunium and plutonium should prove especially important in characterizing the metallurgical systematics of the actinides.

SUMMARY

X-ray data for eleven binary intermetallic compounds of plutonium have been obtained. These are listed in Appendix I, and are compared with American results from the Los Alamos Laboratory (5). Russian results (9) for $PuBe_{13}$, $PuFe_2$, $PuMn_2$, and $PuNi_2$ are included in the Appendix.

Nine of the compounds are isostructural with the corresponding uranium compounds. $PuAl_3$ has a structure not previously reported. $PuAg_3$ appears also to have a new structure but a complete structure determination was not carried out.

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THEORY OF THE TRANSIENT PHASE IN KINETICS, WITH SPECIAL REFERENCE TO ENZYME SYSTEMS

II. THE CASE OF TWO ENZYME–SUBSTRATE COMPLEXES[1]

By Ludovic Ouellet and Keith J. Laidler

ABSTRACT

A theoretical treatment is worked out for the kinetic scheme

$$E + S \rightleftarrows (ES)_1 \rightleftarrows (ES)_2 \rightarrow E + P$$

in which two enzyme–substrate complexes are formed consecutively. The steady-state rate equations are obtained, and equations are given for the transient phase subject to the condition that the substrate concentration is greatly in excess of that of the enzyme. Some kinetic consequences of the resulting equations are discussed.

In a previous paper (3) the reaction scheme

$$E + S \rightleftarrows ES \rightarrow E + P$$

has been considered from the standpoints of the conditions under which the steady-state theory applies, and of the kinetic behavior during the transient phase which exists prior to the establishment of the steady state. Since several recent publications (1, 2, 4) have referred to the possibility that there may be several enzyme–substrate complexes formed in consecutive reactions we have thought it of interest to consider briefly the steady-state and transient-phase equations for such a system. We have confined our considerations to the case of two enzyme–substrate complexes, since the transient-phase equations become very complicated if more complexes are assumed.

THEORY

The system under consideration is

$$\underset{e_0-y_1-y_2}{E} + \underset{s_0}{S} \overset{k_1}{\underset{k_{-1}}{\rightleftarrows}} \underset{y_1}{(ES)_1} \overset{k_2}{\underset{k_{-2}}{\rightleftarrows}} \underset{y_2}{(ES)_2} \overset{k_3}{\rightarrow} \underset{e_0-y_1-y_2}{E} + \underset{p}{P}.$$

It is to be noted that the complexes are formed reversibly, the final products irreversibly. The concentrations of the various substances are indicated above. As discussed in the previous paper (3) the substrate concentration can be assumed to be essentially s_0 during the transient phase provided that the initial concentration of substrate is much greater than that of the enzyme.

The kinetic equations applicable to the above system are

$$[1] \qquad \dot{y}_1 = k_1 s_0 (e_0 - y_1 - y_2) - (k_{-1} + k_2) y_1 + k_{-2}\, y_2$$

$$[2] \qquad \dot{y}_2 = k_2\, y_1 - (k_{-2} + k_3) y_2$$

$$[3] \qquad \dot{p} = k_3\, y_2.$$

[1]*Manuscript received October 17, 1955.*
Contribution from the Department of Chemistry, The University of Ottawa, Ottawa, Canada.

Steady State

The steady-state equations are obtained by setting $\dot{y}_1$ and $\dot{y}_2$ equal to zero and solving Eqs. [1] and [2]. The solution for y_2 is

$$[4] \qquad y_2 = \frac{k_1 k_2 e_0 s_0}{k_1(k_{-2}+k_2+k_3)s_0+(k_{-1}k_{-2}+k_{-1}k_3+k_2k_3)}$$

and the rate is therefore

$$[5] \qquad \dot{p} = \frac{k_1 k_2 k_3 e_0 s_0}{k_1(k_{-2}+k_2+k_3)s_0+(k_{-1}k_{-2}+k_{-1}k_3+k_2k_3)}.$$

This may be expressed in the familiar form

$$[6] \qquad \dot{p} = \frac{V s_0}{K_m+s_0}$$

where V, the maximum rate, is given by

$$[7] \qquad V = \frac{k_2 k_3 e_0}{k_{-2}+k_2+k_3}$$

and K_m, the Michaelis constant, is

$$[8] \qquad K_m = \frac{k_{-1}k_{-2}+k_{-1}k_3+k_2k_3}{k_1(k_{-2}+k_2+k_3)}.$$

If k_3 is very large the second complex $(ES)_2$ has no stable existence, and the relationships then reduce to the familiar forms

$$[9] \qquad V = k_2 e_0$$

$$[10] \qquad K_m = (k_{-1}+k_2)/k_1$$

applicable to the case of the single complex.

The Transient Phase

The kinetic equations for the transient phase are obtained as follows. Elimination of y_1 between Eqs. [1] and [2] gives rise to

$$[11] \qquad \ddot{y}_2+\dot{y}_2(k_1 s_0+k_{-1}+k_2+k_{-2}+k_3) + y_2[k_1(k_2+k_{-2}+k_3)s_0+k_{-1}k_{-2}+k_2 k_3]-k_1 k_2 s_0 e_0 = 0.$$

This may be written as

$$[12] \qquad \ddot{y}_2+P\dot{y}_2+Qy_2-R = 0.$$

The solution of this is

$$[13] \qquad y_2 = +(R/Q)+M \exp\{\tfrac{1}{2}[-P+\sqrt{(P^2-4Q)}]\,t\}+N \exp\{\tfrac{1}{2}[-P-\sqrt{(P^2-4Q)}]t\}$$

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where M and N are constants to be determined from the boundary conditions. The condition $t = 0$, $y_2 = 0$ leads to

$$M+N = -R/Q \tag{14}$$

and $t = 0$, $\dot{y}_2 = 0$ leads to

$$\frac{M}{N} = \frac{P+\sqrt{(P^2-4Q)}}{-P+\sqrt{(P^2-4Q)}}. \tag{15}$$

The solution of Eqs. [14] and [15] leads to

$$M = -\frac{R}{Q}\cdot\frac{P+\sqrt{(P^2-4Q)}}{-P+\sqrt{(P^2-4Q)}} \tag{16}$$

and

$$N = -\frac{R}{Q}\cdot\frac{\sqrt{(P^2-4Q)}-P}{2\sqrt{(P^2-4Q)}}. \tag{17}$$

The expression for y_2 is therefore

$$y_2 = \frac{R}{Q}\left[1-\frac{P+\sqrt{(P^2-4Q)}}{2\sqrt{(P^2-4Q)}}\exp\{\tfrac{1}{2}[-P-\sqrt{(P^2-4Q)}]t\}\right. \\ \left.-\frac{\sqrt{(P^2-4Q)}-P}{2\sqrt{(P^2-4Q)}}\exp\{\tfrac{1}{2}[-P-\sqrt{(P^2-4Q)}]t\}\right]. \tag{18}$$

This is of the form

$$y_2 = (R/Q)+M\,e^{Ft}+N\,e^{Gt} \tag{19}$$

where R, Q, M, and N are defined above and F and G are given by

$$F=\tfrac{1}{2}[P-\sqrt{(P^2-4Q)}] \tag{20}$$

$$G=\tfrac{1}{2}[+P+\sqrt{(P^2-4Q)}]. \tag{21}$$

Insertion of Eq. [19] in Eq. [3] followed by integration then gives rise to the following expression for p as a function of time:

$$p = \frac{k_3R}{Q}t+\frac{k_3M}{F}(e^{-Ft}-1)+\frac{k_3N}{G}(e^{-Gt}-1). \tag{22}$$

The general form of this relationship is as shown in Fig. 1. When t is sufficiently large the exponential terms vanish (since F and G are necessarily positive) and the equation reduces to

$$p = \frac{k_3R}{Q}t-\frac{k_3M}{F}-\frac{k_3N}{G}. \tag{23}$$

This linear relationship between p and t corresponds to the establishment of the steady state. If this linear portion of the curve is extrapolated back to the time axis the intercept, which may be referred to as the induction period for the reaction, is given by

$$\tau = \frac{Q}{R}\left(\frac{M}{F}+\frac{N}{G}\right). \tag{24}$$

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If the expressions for F, G, M, N, Q, and R are inserted into this relationship it is found that

$$[25] \qquad \tau = P/Q$$

$$[26] \qquad = \frac{k_1 s_0 + k_{-1} + k_2 + k_{-2} + k_3}{k_1(k_2 + k_{-2} + k_3)s_0 + k_{-1}k_{-2} + k_1 k_3 + k_2 k_3}.$$

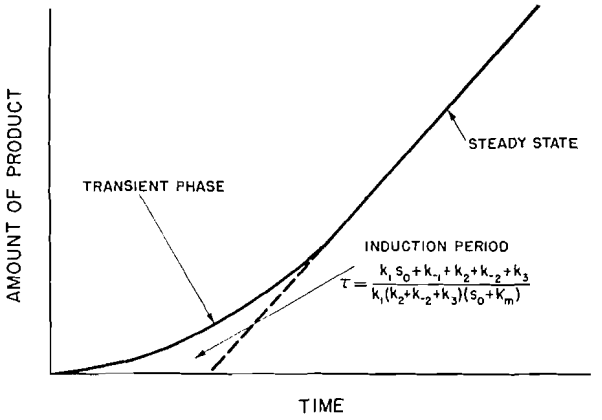

FIG. 1. Schematic plot of amount of product against time, for the case in which there are two successive enzyme–substrate complexes.

Using Eq. [8] this may be written as

$$[27] \qquad \tau = \frac{k_1 s_0 + k_{-1} + k_2 + k_{-2} + k_3}{k_1(k_2 + k_{-2} + k_3)(s_0 + K_m)}.$$

Periodic Solutions

The interesting possibility of periodic behavior can be shown to arise if $P^2 - 4Q$ is less than zero. Algebraic analysis shows that this can happen only if $k_2 > k_{-1}$. The necessary conditions can then be written as

$$[28] \quad k_2 + k_{-2} + k_3 - 2\sqrt{[(k_2 - k_{-1})k_3]} < k_1 s_0 + k_{-1} < k_2 + k_{-2} + k_3 + \sqrt{[(k_2 - k_{-1})k_3]}.$$

Under these conditions, Eq. [18] can be written as

$$[29] \quad y_2 = \frac{R}{Q} - \frac{R}{Q}\left[\exp -\frac{Pt}{2}\right]\left(\cos\frac{\sqrt{(4Q - P^2)}}{2} \cdot t + \frac{RP}{Q\sqrt{(4Q - P^2)}} \sin\frac{\sqrt{(4Q - P^2)}}{2} \cdot t\right).$$

This is the equation of a damped periodic variation, the period T of which is given by

$$[30] \qquad T = 4\pi/\sqrt{(4Q - P^2)}.$$

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Eqs. [25] and [30] yield, in terms of the measurable quantities τ and T,

$$Q = \frac{2 \mp 2\sqrt{[1-(4\pi^2\tau^2/T^2)]}}{\tau^2} \qquad [31]$$

and

$$P = \frac{2 \mp 2\sqrt{[1-(4\pi^2\tau^2/T^2)]}}{\tau}. \qquad [32]$$

P and Q are not complex quantities, so that

$$T \geqslant 2\pi\tau \qquad [33]$$

is a necessary relation between the measurable quantities T and τ. The fact that T must be so much greater than τ makes it difficult to detect the periodicity experimentally. In ideal cases a plot of P against s, by extrapolation to $s = 0$, gives

$$P_{s=0} = k_{-1}+k_2+k_{-2}+k_3 \qquad [34]$$

and the slope of the line will give k_1 directly. A similar plot for Q yields

$$Q_{s=0} = k_{-1}(k_{-2}+k_3)+k_2\,k_3 \qquad [35]$$

and the slope of the line is $k_1(k_2+k_{-2}+k_3)$. Equations [7], [8], [34], [35] and the slopes of P vs. s_0 and Q vs. s_0 provide six relations to determine five constants.

DISCUSSION

Certain special cases of the above equations are of some interest. In the first place, in the event that k_3 is very large (i.e. that the complex $(ES)_2$ has only a fleeting existence) the induction period is given by

$$\tau = 1/[k_1(s_0+K_m)]. \qquad [36]$$

This equation was previously quoted by Gutfreund (2), and it follows directly from Eq. [48] of the previous paper (3). Since Eq. [36] is of the same form as Eq. [27] it is clearly not possible to tell, from a study of the induction period, anything about the existence of the second complex.

Another result of interest is obtained if s_0 is sufficiently large. The induction period is then

$$\tau = 1/(k_2+k_{-2}+k_3). \qquad [37]$$

A plot of $\tau(s_0+K_m)$ against s_0 would give this quantity as its slope. In the event that one of these three rate constants is much larger than the others the induction period is thus, at high s_0, equal to the reciprocal of that constant.

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VAPOR PRESSURES OF AQUEOUS SOLUTIONS OF SILVER NITRATE, OF AMMONIUM NITRATE, AND OF LITHIUM NITRATE[1]

By A. N. Campbell, J. B. Fishman, G. Rutherford, T. P. Schaefer,[2] and L. Ross

ABSTRACT

This paper is devoted to the direct determination of the vapor pressures of solutions of the nitrates of silver, of ammonium, and of lithium, at temperatures varying from 30° C. to 105° C. and at concentrations varying from 10 to 85 weight % (for lithium nitrate, the limited solubility precluded measurements beyond 65%). From the vapor pressures, the enthalpies of evaporation of water (by a modification of the Clapeyron–Clausius equation), the differential heats of dilution, and the activities of water (as compared with the mole fractions of the solvent) have been calculated. From the results we conclude that the water of hydration of the ammonium and silver ions (if, indeed, these ions are hydrated at all) is very loosely attached, while that of the lithium ion is strongly bound.

The present work was undertaken because it was thought that a knowledge of the vapor pressures at a series of temperatures would yield the heat of evaporation of water from solutions of different concentrations and hence throw some light, if only of a qualitative nature, on the firmness with which the different ions held their water of hydration. As the concentration of an electrolytic solution is increased there will be fewer molecules of water left for ionic hydration; at extremely high concentration there will be strong competition for the remaining water molecules. Using the concept of Stokes and Robinson (8) that the ions adsorb layers of water molecules in accordance with the Brunauer, Emmet, and Teller equation, it should become progressively more difficult to strip away the successive layers of water surrounding the ions; the last and most firmly bound layer should require a large amount of energy to remove it. Application of the Clapeyron–Clausius equation (though not in its normal form: see Discussion) to the vapor pressures of concentrated solutions should give the heat of evaporation and hence, perhaps, a measure of the difficulty of removing water from the ions.

The problem of finding vapor pressures was first attempted by finding boiling points at different fixed pressures. After spending a year, however, on this method of attack we abandoned it because we found that, although we could control pressure and boiling point to any desired degree of constancy, we had no certainty as to the composition of the equilibrium liquid. Indeed, the work about to be described showed that we occasionally had composition errors equivalent to an error of 0.5° in boiling point.

Because of this uncertainty in the composition variable of the boiling point method, we decided to turn to a method in which the composition factor would be known and invariable. The direct determination of vapor pressure in a closed system offers such a method. The loss of water by evaporation to produce one atmosphere pressure in a closed system is negligible, even in the strongest solutions used.

[1]*Manuscript received October 3, 1955.*
Contribution from the Chemistry Department, University of Manitoba, Winnipeg, Manitoba.
[2]*Holder of a N.R.C. Bursary.*

There has been surprisingly little experimental work done on the vapor pressure of aqueous electrolytic solutions, especially over a range of temperature. Most of that which has been done is confined to the isopiestic measurement of vapor pressures for the determination of activity at 25° C.

Our vapor pressure measurements have been utilized to calculate the heat of evaporation of water from the various solutions, the heat of dilution, and the activity of water as given by the ratio p/p_0.

EXPERIMENTAL PROCEDURE

The sources and purity of our materials have frequently been described elsewhere (1). All solutions were made up by direct weighing, using salts which, after purification, had been thoroughly dried; the lithium nitrate was always fused before use. For the determination of the vapor pressures of the more dilute solutions the differential manometer of Hartung (4) was used. It was possible to use this up to concentrations of 60% by weight for silver nitrate solutions but only up to 40% concentration for lithium nitrate. In the differential manometer one limb contains pure water and the other the solution.

Fig. 1 represents Hartung's apparatus as used by us. The method of use is described by Hartung but certain modifications are mentioned here. For instance, since we used mineral oil in our thermostat and worked up to temperatures of 105°, it was impossible to use ordinary rubber in the thermostat and neoprene was used for the bung through which the long limb of the mano-

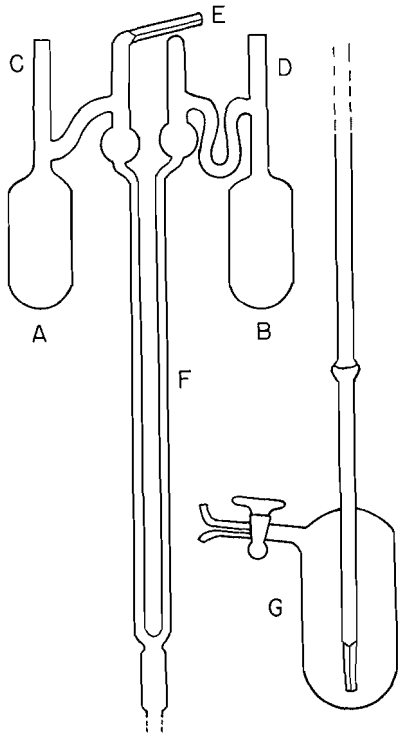

Fig. 1.

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meter passes. The long limb was also severed, about 10 cm. above the mercury reservoir, and a ball and socket joint introduced; this facilitated the installation and dismantling of the apparatus, which had to be done every time a new solution was introduced. A little silicone oil was allowed to float on top of both mercury levels in the manometer. This had the dual advantage of preventing the condensation of small amounts of water on the mercury surfaces (which, we found, produced distortion in the field of vision of the cathetometer) and, when silver nitrate solutions were used, of preventing mercury vapor entering the solutions and causing decomposition, as it does very readily.

The necessity of removing the last trace of air in all vapor pressure measurements is well known, and for this purpose the procedure adopted was to freeze both bulbs in dry ice. The mercury level was then lowered and both bulbs evacuated continuously for the space of half an hour. The mercury level was then raised and the contents of the bulbs allowed to thaw. The above procedure was repeated at least four times. Finally the capillary leading to the pump was sealed off and the contents allowed to thaw for the last time. The solution was then agitated to ensure homogeneity.

With the more concentrated solutions (70% by weight for silver nitrate, 40% for lithium nitrate) it was impossible to use the differential manometer, since the limbs of the U-tube were only 20 cm. long, and with highly concentrated solutions at higher temperatures the difference in vapor pressure from that of water became greater than 20 cm. of mercury. A direct barometric apparatus therefore became necessary.

The apparatus is shown in Fig. 2. Dissolved air was removed by the same treatment as already described. In the more concentrated solutions now used,

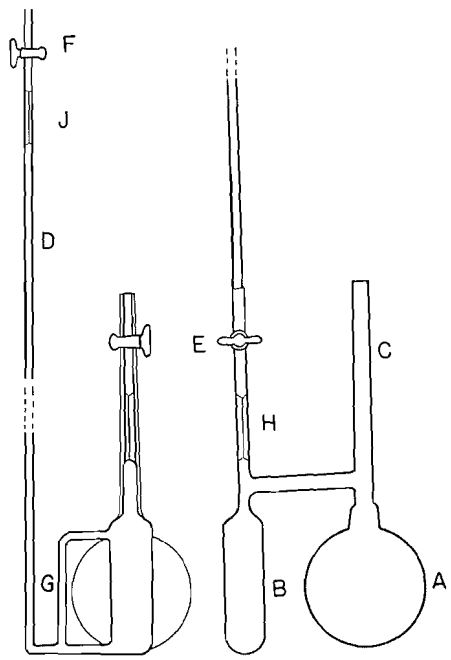

Fig. 2.

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the 'salting-out' effect rendered the solubility of air much less and the difficulty of removing dissolved air was proportionately reduced.

All manometers were completely immersed in a tall rectangular copper tank furnished with glass sides. Because the thermostatic fluid was mineral oil it was necessary to use Buna-N rubber as gasket material for the glass windows. Measurements were made between 30° C. and 105° C. The usual procedure of using an immersion heater to keep temperature slightly below the operating temperature and controlling an electric light bulb as the source of extra heat, together with the use of three stirrers, gave a temperature fluctuation of not more than ±0.02° C., over the whole range of temperature.

Two cathetometers were used to measure differences in mercury levels, one a short range instrument which could be read to 0.01 mm., and another of greater range which could be read to 0.1 mm. Successive readings showed that it required about two hours to obtain equilibrium at the lower temperatures, while half an hour sufficed at the higher temperatures. All mercury columns were reduced to 0° C. The probable error does not exceed 0.2% and this makes the data good enough for most purposes.

EXPERIMENTAL RESULTS

The experimental results are given in Table I.

TABLE I

THE VAPOR PRESSURES OF SOLUTIONS OF SILVER NITRATE, OF AMMONIUM NITRATE, AND OF LITHIUM NITRATE AT DIFFERENT TEMPERATURES

Silver nitrate			Ammonium nitrate			Lithium nitrate		
Conc., wt. %	Temp., ° C.	Press., mm. Hg	Conc., wt. %	Temp., ° C.	Press., mm. Hg	Conc., wt. %	Temp., ° C.	Press., mm. Hg
9.98	30.06	31.64	10.00	30.00	31.51	10.00	30	30.48
	40.00	54.63		40.00	54.48		40	52.57
	50.00	91.37		50.00	90.70		50	87.83
	60.00	147.4		60.00	145.90		60	141.76
	70.00	230.4		70.00	227.17		70	221.40
	80.00	349.8		80.00	344.10		80	335.90
	90.00	517.5		90.00	508.2		90	497.20
	101.00	774.8		100.00	733.2		100	718.35
				101.40	770.5		102	771.08
19.98	30.06	31.57	20.00	30.00	30.90	20.00	30	27.83
	40.00	54.36		40.00	53.84		40	48.35
	50.00	90.81		50.00	88.94		50	80.67
	60.00	146.0		60.00	141.8		60	130.60
	70.00	227.5		70.00	219.3		70	203.93
	80.00	344.9		80.00	330.5		80	309.12
	90.00	509.0		90.00	486.5		90	456.21
	101.00	760.7		100.00	699.8		100	658.05
				102.00	750.6		105	784.04
30.00	30.00	30.30	30.00	30.00	30.43	30.00	30	23.08
	40.00	52.63		40.00	52.00		40	40.22
	50.00	87.77		50.00	84.78		50	66.79
	60.00	141.3		60.00	134.7		60	109.42
	70.00	220.6		70.00	208.2		70	171.32
	80.00	334.8		80.00	313.0		80	261.16
	90.00	495.0		90.00	459.6		90	388.41
	102.00	767.5		100.00	659.9		100	562.25
				104.00	758.4			

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TABLE I (*Concluded*)

Silver nitrate			Ammonium nitrate			Lithium nitrate		
Conc., wt. %	Temp., ° C.	Press., mm. Hg	Conc., wt. %	Temp., ° C.	Press., mm. Hg	Conc., wt. %	Temp., ° C.	Press., mm. Hg
40.00	30.00	29.50	40.00	30.00	26.25	40.00	30	19.18
	40.00	51.18		40.00	45.30		40	33.11
	50.00	85.40		50.00	75.09		50	55.73
	60.00	137.5		60.00	120.8		60	89.34
	70.00	214.5		70.00	188.0		70	140.45
	80.00	325.7		80.00	284.6		80	215.06
	90.00	481.4		90.00	420.0		90	320.30
	103.00	772.8		100.00	604.3		100	463.97
				105.71	736.9		105	556.78
50.00	30.00	28.68	50.00	30.00	25.65	50.00	30	13.59
	40.00	49.78		40.00	43.39		40	23.37
	50.00	82.95		50.00	71.68		50	39.93
	60.00	133.6		60.00	113.4		60	64.66
	70.00	208.6		70.00	176.0		70	102.21
	80.00	316.3		80.00	265.7		80	157.20
	90.00	466.9		87.91	358.9		90	236.10
	103.00	749.1		100.00	555.7		104	400.57
59.29	31.04	29.33	60.00	30.00	21.72	57.28	30	9.21
	40.09	47.87		40.00	36.96		40	16.61
	50.14	79.70		50.00	61.54		50	28.49
	60.28	129.2		60.00	98.36		60	46.86
	70.37	202.7		70.00	152.8		70	75.77
	80.50	308.6		80.00	231.0		80	118.25
	90.56	457.5		90.00	339.5		90	179.31
	100.65	662.0		100.00	486.7		100	264.20
	105.60	787.1					105	319.87
69.99	30.00	26.15	70.00	40.00	31.62	64.953	30	
	40.00	45.88		50.00	52.10		40	11.14
	50.00	75.79		60.00	82.20		50	19.01
	60.00	122.0		70.00	128.6		60	31.74
	70.00	189.6		80.00	193.8		70	50.77
	80.00	286.2		90.00	285.6		80	79.77
	90.00	421.5		100.00	405.5		90	122.22
	100.00	606.6					100	182.06
							105	221.34
80.05	60.00	107.2	80.00	60.00	63.82			
	65.00	134.2		70.00	98.13			
	70.00	166.8		80.00	146.4			
	75.00	206.2		90.00	213.5			
	80.00	252.6		100.00	304.8			
	85.00	307.9						
	90.00	372.4						
	95.00	447.9						
	100.00	534.8						
85.07	75.00	183.1	90.00	100.00	201.2			
	80.00	223.8		105.00	240.2			
	82.00	246.6		110.00	281.9			
	85.00	271.8		115.00	330.0			
	87.50	298.8		120.00	385.7			
	90.00	328.6		125.00	445.7			
	92.50	360.8		130.00	512.0			
	100.00	471.6						
90.00	120.00	716.1						
	124.80	820.2						
	126.58	866.3						
	130.00	950.4						

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DISCUSSION

In order to obtain ΔH_1 (the molar enthalpy of evaporation of water from the different solutions) the following procedure was adopted: Using the Clapeyron–Clausius equation, in its classical form, the calculation must be restricted to a small range of temperature over which ΔH may be regarded as constant; such a restriction magnifies the experimental error. A very useful application of the Clapeyron–Clausius equation for the correlation of vapor pressure and latent heat data has, however, been given by Othmer (7). Using the symbols ΔH_1 and ΔH_2 for the molar enthalpies of evaporation of water from solution and from pure water respectively and rearranging the differential form of the Clapeyron equation, the following expression results:

$$[1] \qquad (1/\Delta H_1)(dP_1/P_1) = dT/RT^2.$$

The same expression may be written for any other material at the same temperature as:

$$[2] \qquad (1/\Delta H_2)(dP_2/P_2) = dT/RT^2.$$

P_1 and P_2 are the vapor pressures of the two substances at the same temperature T. Equating equations [1] and [2] and rearranging, equation [3] is obtained:

$$[3] \qquad dP_1/P_1 = (\Delta H_1/\Delta H_2)(dP_2/P_2).$$

With the usual assumptions as to the vapor being an ideal gas and the volume of the condensed phase being negligible, one obtains, in logarithmic form,

$$[4] \qquad d(\log P_1)/d(\log P_2) = \Delta H_1/\Delta H_2.$$

If $\Delta H_1/\Delta H_2$ is considered constant, equation [4] may be integrated to give equation [5],

$$[5] \qquad \log P_1 = (\Delta H_1/\Delta H_2) \log P_2 + C.$$

Hence, if the logarithm of the vapor pressure, P_1, of a solution is plotted against the logarithm of the vapor pressure of water, P_2, at the same temperature, a straight line results which has for its slope the ratio of the molar enthalpies of evaporation. This line is straight if the ratio $\Delta H_1/\Delta H_2$ is constant over the temperature range in question and this is reasonably near the truth for water and aqueous solutions. Knowing the value of the ratio, and that of the latent heat of evaporation of pure water, ΔH_1, the latent heat of evaporation of water from solution is obtained. The best data for the latent heats of evaporation of water, and for vapor pressure, are contained in a paper by Goff and Gratch (3); they give an equation for vapor pressure of water in terms of temperature, which we have used throughout. The slopes of log P_1 versus log P_2 were calculated analytically by the method of moments instead of by the more inaccurate graphical method.

In Table II are given the values of ΔH_1, the latent heat of evaporation of water from the various solutions, for a mean temperature of 50° C. For this temperature we have taken ΔH_2, the heat of evaporation of pure water, to be 10,245 cal.; this is the average of several direct calorimetric determinations by Johnson and Molstad (6). An examination of Table II shows that, for silver nitrate, ΔH for solution is not much different from that for pure water. The

slight difference is positive and increases with increasing concentration, i.e., less heat is required to evaporate water from solution than from pure water. Similar results have been obtained before. Thus, Hirschler (5) showed that the vapor pressures of certain saturated aqueous solutions, when plotted as

TABLE II

THE SLOPES $\Delta H_1/\Delta H_2$ OF LOG P_1 VERSUS LOG P_2, AND THE VALUE OF ΔH_1, AT 50° C. (ΔH_2 = 10,245 CAL./MOLE)

Conc., wt. %	Slope $\Delta H_1/\Delta H_2$	ΔH_1	$\Delta H_2-\Delta H_1$
	Silver nitrate		
9.98	0.9982	10227	18
19.98	0.9929	10172	73
30.00	0.9960	10204	41
40.00	0.9958	10202	43
50.00	0.9948	10192	53
59.29	0.9948	10192	53
69.99	0.9895	10138	107
80.05	0.9893	10135	110
85.07	0.9799	10039	206
	Ammonium nitrate		
10.00	0.9916	10158	87
20.00	0.9811	10047	198
30.00	0.9702	9948	297
40.00	0.9889	10130	115
50.00	0.9613	9832	413
60.00	0.9817	10054	191
70.00	0.9765	9999	246
80.00	0.9611	9834	411
90.00	0.9523	9759	486
	Lithium nitrate		
10.00	0.9967	10211	34
20.00	0.9969	10213	32
30.00	1.0078	10325	− 79
40.00	1.0063	10310	− 64
50.00	1.0225	10476	−225
57.28	1.0585	10844	−566
64.953	1.0700	10962	−670

log P vs. $1/T$, give straight lines parallel to a similar plot for water. Since $\Delta H_2-\Delta H_1$ is a small positive quantity and increases with increasing concentration, this means that heat is adsorbed when a mole of water is added to a large amount of solution (differential heat of dilution) and this amount of heat increases with increasing concentration. For ammonium nitrate, the differential heat of dilution is also positive, but rather more pronounced, amounting to half a kilocalorie at the highest concentration. For lithium nitrate the heat of dilution is negative. Heat is evolved when lithium nitrate solutions are diluted and this seems to be in harmony with the accepted belief in the strongly hydrated lithium ion.

In Table III, the activity of the water in solution, derived from the vapor pressure and the corresponding vapor pressure of pure water, is compared with the mole fraction of water (calculated on the assumption of non-ionized salt).

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For silver nitrate, the agreement is surprisingly good between the mole fraction and the activity coefficient and it is essentially independent of temperature, i.e., Raoult's law is obeyed, throughout the concentration range, far more closely than it should be for a solution of an electrolyte. Campbell and Kartz-

TABLE III

THE ACTIVITY OF WATER P/P_0 IN SOLUTIONS AT VARIOUS CONCENTRATIONS AND TEMPERATURES

Conc., mole fraction of water*	Temperature (° C.)							
	30	40	50	60	70	80	90	100
Silver nitrate								
0.9883	.9906	.9872	.9872	.9860	.9855	.9845	.9842	
0.9742	.9884	.9823	.9811	.9766	.9731	.9707	.9680	
0.9565	.9519	.9510	.9482	.9452	.9435	.9423	.9414	
0.9340	.9268	.9248	.9226	.9197	.9175	.9167	.9156	
0.9041	.9010	.8995	.8962	.8936	.8922	.8902	.8880	
0.8017	.8216	.8291	.8188	.8161	.8109	.8055	.8016	
0.7015				.7171	.7134	.7109	.7083	
0.6234						.6299	.6250	
Ammonium nitrate								
0.9756	.9901	.9845	.9799	.9759	.9717	.9686	.9663	.9648
0.9467	.9709	.9729	.9609	.9486	.9380	.9304	.9251	.9199
0.9120	.9560	.9398	.9160	.9012	.8905	.8810	.8739	.8683
0.8695	.8248	.8187	.8113	.8082	.8041	.8009	.7987	.7951
0.8163	.8059	.7841	.7745	.7590	.7528	.7478	.7392	.7312
0.7478	.6825	.6679	.6649	.6581	.6537	.6502	.6456	.6404
0.6557		.5714	.5629	.5500	.5498	.5455	.5432	.5335
0.5262				.4270	.4197	.4120	.4060	.4011
Lithium nitrate								
0.9719	.9577	.9500	.9490	.9485	.9470	.9455	.9455	.9452
0.9387	.8743	.8737	.8716	.8738	.8723	.8701	.8675	.8659
0.8993	.7251	.7269	.7216	.7321	.7328	.7351	.7386	.7398
0.8518	.6027	.5983	.6021	.5977	.6007	.6053	.6091	.6105
0.7928	.4269	.4224	.4314	.4326	.4372	.4425	.4490	
0.7406	.2893	.3009	.3078	.3135	.3241	.3328	.3410	.3476
0.67373		.2013	.2054	.2123	.2172	.2245	.2324	.2396

**Calculated on the assumption of no ionization, i.e., the weight of silver nitrate is divided by the molecular weight.*

mark (2) have calculated the extent of ion-pair formation in silver nitrate solutions, but this is far from complete at concentrations for which the calculation is valid and therefore it is impossible to account for the above observation on the assumption that silver nitrate is only slightly ionized. For ammonium nitrate, however, the activity drops markedly with rising temperature and, for concentrations of 80 and 90% (mole fractions of 0.6557 and 0.5262 water) the activity is much lower than the mole fraction. For lithium nitrate, the discrepancy between activity and mole fraction is still greater. Since activity and concentration are related, it would appear that the concentration of (free) water is somewhat less in ammonium nitrate solutions than the mole fraction would imply and, in lithium nitrate solutions, very much less. This

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can be accounted for on the assumption that the silver ion is not (or very feebly) hydrated, the ammonium ion a little more, and the lithium ion very strongly hydrated.

Finally, in Fig. 3, the vapor pressures of all three electrolytes, at different temperatures, have been plotted against mole fraction of solute. The figure brings out very clearly the fact that, at corresponding mole fraction and

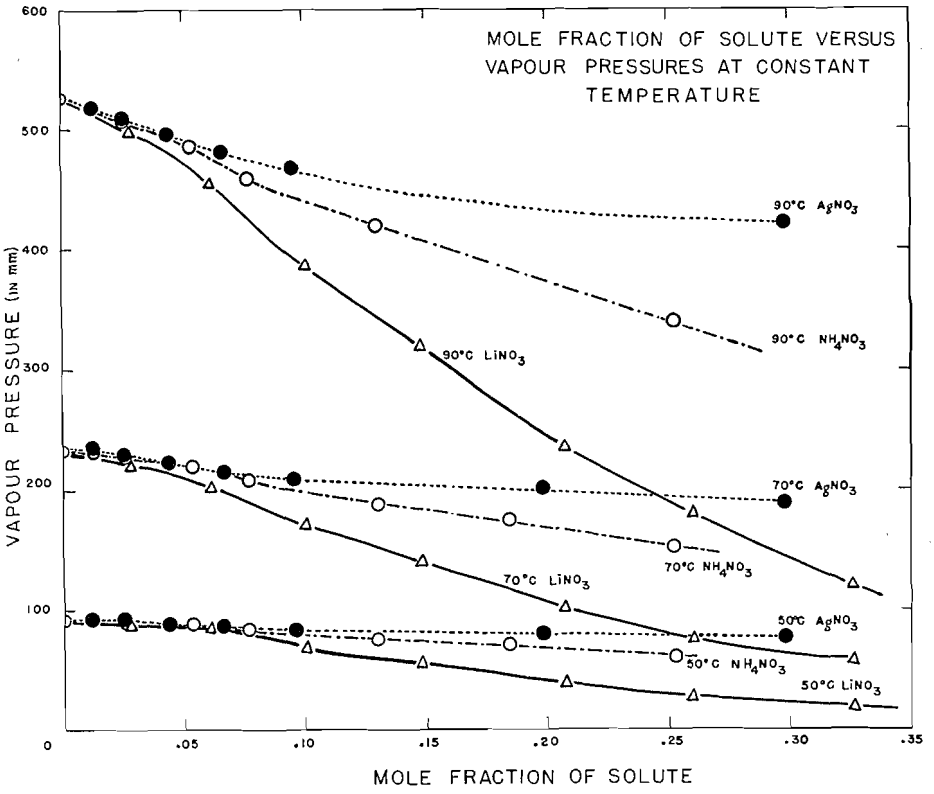

Fig. 3.

temperature, the vapor pressures of the lithium nitrate solutions are much lower than those of the silver nitrate and ammonium nitrate solutions. The most obvious explanation of this is the one given above, viz. that the lithium ion holds its water of hydration much more firmly than do the silver and ammonium ions. The high viscosity of lithium nitrate solutions points in the same direction.

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THE NUMBER OF POLYPEPTIDE CHAINS IN BOVINE PLASMA ALBUMIN[1]

By M. E. Reichmann[2] and J. Ross Colvin

ABSTRACT

The molecular weight of performic acid oxidized bovine plasma albumin, dispersed in 0.08 *M* borate + 0.2 *M* sodium chloride buffer, pH 7.4, was estimated as 30,000 by light-scattering and sedimentation equilibrium methods, 19,000 by osmotic pressure. Sedimentation velocity analyses and electrophoresis showed that the component polypeptide chains of the material are similar in mass and charge density so the polydispersity must be attributed to labile aggregates. The results indicate that here are at least three and probably four similar polypeptide chains in the molecule of native bovine plasma albumin, held together by disulphide bonds.

INTRODUCTION

Knowledge of the number of polypeptide chains in a protein molecule is prerequisite to an understanding of its structure but unequivocal data are available for only a few of these substances (5). Even for readily available bovine plasma albumin (B.P.A.) information is scanty. Previous estimates from end group analyses (33, 37), or from viscosity measurements after the disulphide links between chains were broken by performic acid (19), agree that the most probable figure is one. However, the first method may be misleading because of terminal substitution, and unequivocal interpretation of the second is difficult. Therefore, the number of polypeptide chains in B.P.A. has been redetermined by estimating the molecular weight of the product of performic acid oxidation (29) of B.P.A. by light-scattering, sedimentation equilibrium, and osmotic pressure techniques. The results were supplemented by sedimentation velocity and electrophoretic measurements.

METHODS AND MATERIALS

Previous studies have shown that the disulphide links between amino acid residues in a protein may be destroyed without significant hydrolysis of the peptide bonds (3, 30). Accordingly, the component polypeptide chains were separated by a modification of Sanger's method of oxidizing disulphide bridges (30) on the assumption that any other covalent links, such as phosphate, (22) were absent.

Five grams of B.P.A. (Armour and Co., Chicago, Lot R370295B) was dissolved in 180 ml. of 90% formic acid and 30 ml. of 30% hydrogen peroxide was added. The reaction was allowed to proceed 25 min. at room temperature, then 50 ml. of 95% ethanol was added and the oxidized protein was precipitated by adding 200 ml. of 5 *M* NaCl. The addition of ethanol prevented frothing and loss of material. After the evolution of oxygen stopped, an additional 400 ml. of 5 *M* NaCl was added to ensure complete precipitation. The

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precipitate was separated from the supernatant liquid by centrifugation, resuspended in water, and dialyzed against distilled water for 36 hr. Analysis of the outer liquid showed that less than 1.5% of the precipitated nitrogen passed through the membrane during dialysis. Similar analysis of the supernatant liquid from centrifugation showed that less than 2.0% of the total nitrogen failed to be precipitated by the salt solution. Finally, the oxidized, dialyzed B.P.A. was freeze dried. Ninety-five per cent of the initial nitrogen was recovered. The slightly yellow, fluffy powder was initially insoluble in water at neutrality to pH 9.5. However, the protein did not reprecipitate when the pH was adjusted to neutrality by dialysis. The oxidized protein was also readily soluble in formamide, and 90% formic acid. Three separate preparations, made as described above, plus one sample oxidized for 60 min. were examined during the study. No differences were observed between any of the preparations.

During the study, it was necessary to oxidize crystalline lysozyme (Armour and Co., Chicago) as above, except that the oxidized protein was precipitated by 180 ml. of saturated Na_2SO_4 per gram of lysozyme and dialysis times were extended in order to remove the sulphate ion completely.

An aliquot of the first preparation of oxidized B.P.A. was hydrolyzed by refluxing in 3 *N* HCl in 50% formic acid for 24 hr. and the hydrolyzate analyzed qualitatively for sulphydryl or disulphide bonds by the methods of Toennies and Kolb (35). Neither cysteine nor cystine was detectable with the nitroprusside reagent or potassium cyanide indicating complete conversion of these two amino acid residues to cysteic acid. Examination of trial preparations which were oxidized at room temperature for 5, 10, 15, and 20 min. showed that complete conversion to cysteic acid required about 20 min. under these conditions.

The free α-amino terminal groups were determined in both native and oxidized B.P.A., using Sanger's technique (29). Only aspartic acid residues were detected in both samples. Attempts to determine the number of aspartic acid residues per protein molecule by this method were unsatisfactory owing to appreciable breakdown of the D.N.P.-aspartic acid. However, for a given set of conditions, the number of N-terminal aspartic acid residues appeared to be equal in oxidized and native B.P.A., thus strengthening the assumption that no peptide bonds were broken during the oxidation reaction.

Protein solutions were prepared by dissolving oxidized B.P.A. in formamide and dialyzing against several changes of the appropriate buffer. Protein concentrations were estimated by micro-Kjeldahl analysis (accuracy, $\pm 1\%$ of the total nitrogen present) assuming the total nitrogen content of the protein to be 16.1% (36).

A Brice and Speiser light-scattering photometer (8) was used to estimate weight average molecular weights. A blue filter (Corning No. 3389, 2.5 mm.) inserted in front of the phototube eliminated fluorescent light. All measurements were made at 4360Å. The refractive index increment, dn/dc, of oxidized B.P.A. was measured in a B.S. differential refractometer. The same value was obtained as that reported for native B.P.A., 0.195 (23), giving $K = 2\pi^2 n_0^2 (dn/dc)^2 / N\lambda^4$ the value of 6.2×10^{-7} (n_0 = refractive index of solvent, N = Avogadro's number, λ = wavelength of light used). All measurements

were made in the standard 30 mm. square cells. Other details of the technique were as described previously (25).

Sedimentation coefficients were estimated from observations in a Spinco ultracentrifuge at 59,780 r.p.m. A one degree adjustment for adiabatic cooling of the rotor (6, 38) was included in the standard corrections of the coefficients to water at 20° (32). Three determinations of the sedimentation coefficient S_{20}, of native B.P.A. in 0.05 *M* phosphate buffer, 0.2 *M* NaCl, pH 6.6, at concentrations 0.33%, 0.50%, and 1.0% gave the values 4.10, 4.08, and 3.91×10^{-13} respectively. These values and their extrapolation to 4.3×10^{-13} at zero concentration are in agreement with previous determinations (21). However, repeated similar determinations of the coefficient of native B.P.A. in 0.08 *M* borate, 0.2 *M* NaCl, yielded a value of S°_{20} of 4.6×10^{-13}. The sedimentation coefficients reported for oxidized B.P.A. in 0.08 *M* borate +0.2 *M* NaCl, pH 7.4, may therefore be 10% too high. Cause of the discrepancy is unknown. In spite of this qualification, the borate buffer was used because of the difficulties of cleaning phosphate or more alkaline buffers for light-scattering.

Archibald (4) has shown that in sedimentation equilibrium experiments the weight average molecular weight may be estimated from the polymer concentrations near the ends of the cell, prior to complete attainment of equilibrium. The method has been applied successfully to bacitracin (24), digitonin (9), and lysozyme (31). In addition, the procedure gives information on polydispersity of the sample since, for heterogeneous samples, the molecular weight at the base of the cell will be higher than at the meniscus and the difference will increase with time. This technique was therefore applied to oxidized B.P.A. The ultracentrifuge and cells were the same as in the sedimentation velocity experiments. Speed of the rotor was 5300 r.p.m. Photographs were taken every four hours in the interval from 12 to 40 hr. From the sedimentation patterns, a function $\delta = (1/rc)\ (dc/dr)$ was calculated (9), (r is the distance of a given point in the cell from the center of rotation, c is the concentration in gm./ml. at that point, and dc/dr is the concentration gradient). The weight average molecular weights at the meniscus and base of the cell were estimated from the extrapolated values of δ by the relation $\delta = M(1-V\rho)/\omega^2RT$. (Here, V is the partial specific volume of the protein, ρ is the density of the solution, ω is the angular velocity, R is the gas constant, T is the absolute temperature, and M is the molecular weight.) Partial specific volume of oxidized B.P.A. was assumed to be the same as that of the native protein, 0.734 (11).

Osmotic pressures were measured at equilibrium using osmometers previously described (13). In some preliminary experiments (26), Visking dialysis bags were used but later proved unsatisfactory because of flexibility. Parloidin (Mallinckrodt Chem. Works) membranes prepared by Adair's method (1) were substituted. Pressures were determined at 7.5±0.1°C. after 16 hr. of equilibration and confirmed after an additional 12 hr. Equilibrium was reached from both sides and the osmotic pressures thus obtained agreed within experimental error.

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Electrophoretic examinations were carried out at 0.15°C. in a Tiselius schlieren apparatus as modified by Longsworth (20). Dialysis for one day against buffer solutions prepared according to Clark's method (10) preceded examination. The pH of each solution was checked by a Beckman Model G pH meter calibrated by commercial standards.

RESULTS

Results typical of the light-scattering data for oxidized B.P.A. in concentrated salt solutions and in water at pH 7.4 are shown in Fig. 1. Kc/R_{90} is plotted as a function of protein concentration where R_{90} is the reduced intensity of

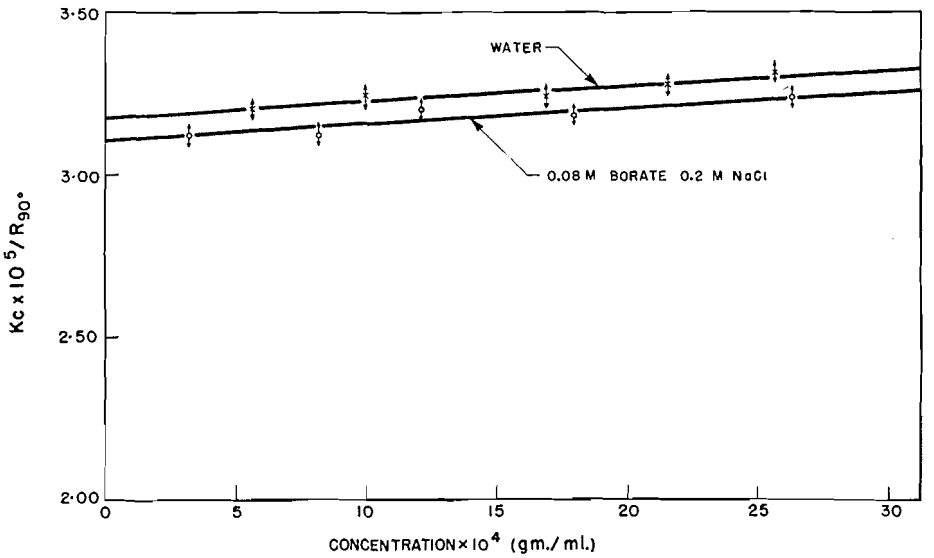

FIG. 1. Light-scattering of oxidized B.P.A. in 0.08 M borate + 0.2 M sodium chloride, and in water, both at pH 7.4.

the light scattered at 90°, K is as defined previously, and c is the concentration of the protein. The extrapolated value of Kc/R_{90} at zero protein concentration is an estimate of the reciprocal of the weight average molecular weight while the slope of the line is proportional to the second virial coefficient (14). The slope is therefore a measure of the net particle interactions.

Two preparations oxidized for 20 min. and one oxidized for 60 min. were studied by light-scattering. All three oxidized samples had identical weight average molecular weights, 32,000±2000. Under the same conditions native B.P.A. had a molecular weight of 77,000 in good agreement with previous results (16).

Results typical of osmotic pressure experiments on the three samples are shown in Fig. 2. Here P/cRT is plotted as a function of concentration; the osmotic pressure, P, being expressed in dyne/cm.^{2}. The extrapolated value of P/cRT at zero protein concentration was $5.2\pm0.4\times10^{-5}$ which corresponds to a number average molecular weight of 19,000±1500. Under the same

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conditions, native B.P.A. had a number average molecular weight of 67,000 in agreement with previous results (18). The difference between this value and that for the weight average molecular weight 77,000 has been attributed to a small proportion of high molecular weight material present in some

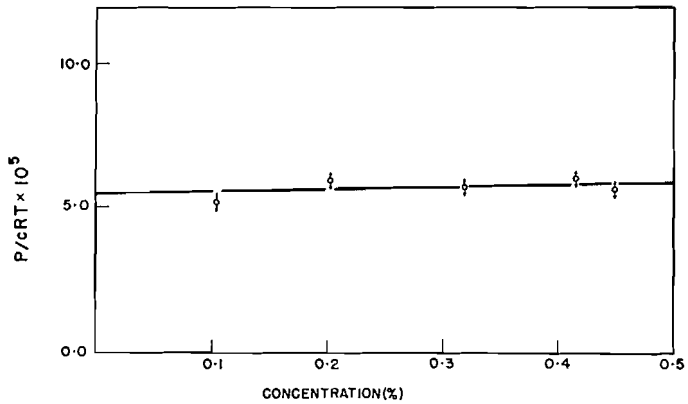

FIG. 2. Osmotic pressure of oxidized B.P.A. as a function of concentration, in 0.08 *M* borate buffer + 0.2 *M* NaCl, pH 7.4.

samples of native B.P.A. (16). Presence of this fraction in our sample was confirmed by sedimentation velocity experiments.

A single peak was observed in sedimentation velocity experiments with oxidized B.P.A. (Fig. 3), which sedimented with a mean coefficient, S°_{20}, of $1.49 \pm 0.05 \times 10^{-13}$ in 0.08 *M* borate, 0.2 *M* NaCl, pH 7.4. The sedimentation

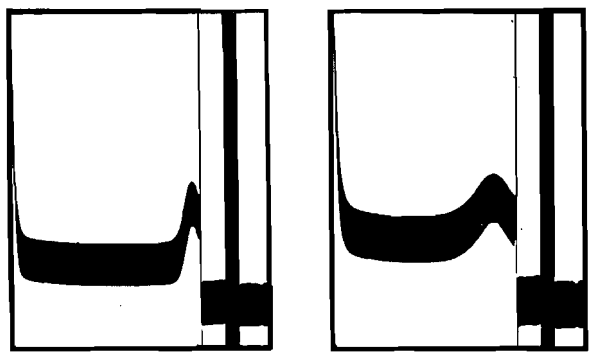

FIG. 3. Sedimentation boundary of oxidized B.P.A. in 0.08 *M* borate + 0.2 *M* NaC pH 7.4.

coefficient was independent of protein concentration over the range 0.3% to 1.0%. The threefold reduction in the value of the coefficient compared with native B.P.A. (21) suggested that oxidation separated the protein into fragments. An estimate of the distribution of the sedimentation coefficients of such fragments of oxidized B.P.A., made by the method of Williams *et al.* (39), showed only a single peak about the mean value. The peak was not

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sharp but the significance which may be attributed to this is doubtful because of inherent uncertainties of extrapolation in the method. A justifiable conclusion is that the sedimentation differences among the molecules are small or else the various types are in rapid equilibrium (2).

Fig. 4 summarizes the data from an experiment using Archibald's approach to sedimentation equilibrium at pH 7.4. The function $(1/rc)(dc/dr)$ is plotted versus r, the distance from the center of rotation, and extrapolated

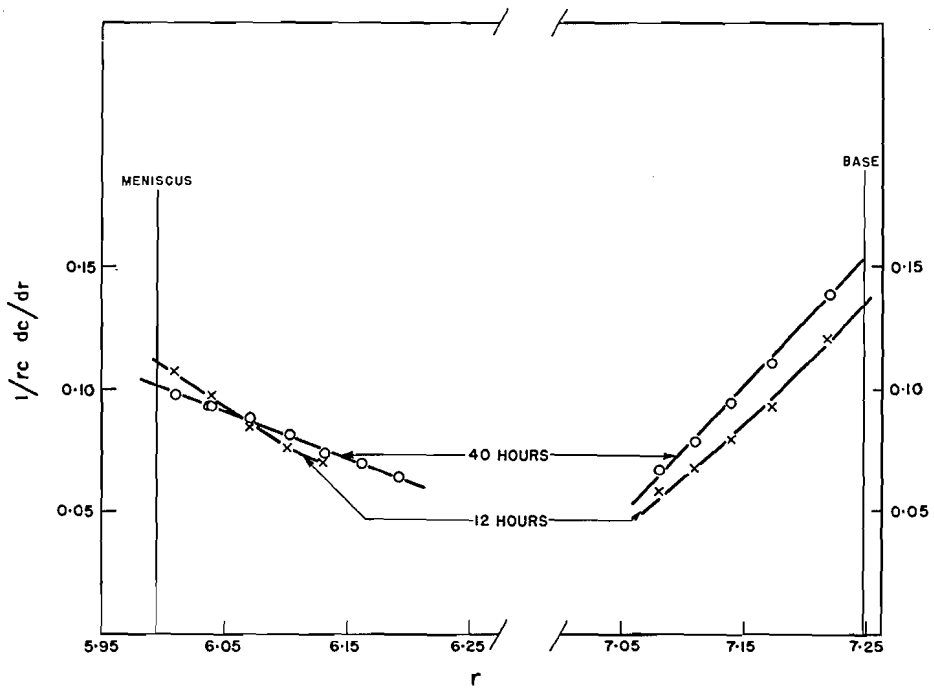

FIG. 4. Archibald's approach to sedimentation equilibrium with oxidized B.P.A. in 0.08 M borate + 0.2 M NaCl, pH 7.4.

to the meniscus and base of the cell. Twelve hours after the beginning of the run the molecular weight at the meniscus was 33,000 and at the base, 40,000. After 40 hr. of sedimentation, the molecular weight decreased to 30,000 at the meniscus and increased to 45,000 at the base. Similar results were obtained at pH 9.0 in aqueous ammonia. These observations are in agreement with those from light-scattering and are consistent with the sedimentation velocity experiments.

Oxidized B.P.A. was examined electrophoretically over the pH range from 4.7 to 7.4 in 0.05 M acetate, phosphate, or borate buffers. Varying concentrations of sodium chloride were added to adjust the field strength. A typical pattern for the material under all conditions is shown in Fig. 5. A single symmetrical peak was observed, suggesting that the charge densities of all the components of oxidized B.P.A. are similar.

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Previous studies of the structure of insulin (30) and of ribonuclease (3) have shown that performic acid under the conditions employed does not hydrolyze peptide bonds appreciably. However these two proteins do not contain the labile tryptophane residue (34) whereas two such residues are found per B.P.A. molecule (36). Performic acid oxidation was therefore

FIG. 5. Ascending and descending electrophoretic boundaries of oxidized B.P.A. in 0.05 *M* acetate buffer, pH 5.5. Field strength 6.3 volts/cm. Time 116 min.

applied to lysozyme (8 tryptophane residues per 15,000 gm. (36)), to see if the single chain of the molecule (17) was broken by the procedure. The oxidized protein was insoluble in water from pH 2.0 to 8.0. Light-scattering measurements of native and oxidized lysozyme were therefore made in 90% formic acid. The molecular weight of the oxidized protein was about five times *higher* than that of the native protein assuming the same values for the refractive index increment in both materials. The data from two experiments using Archibald's approach to sedimentation equilibrium on oxidized and native lysozyme, dissolved in formamide, are summarized in Fig. 6. After 45 hr. at 12,000 r.p.m. the function δ at the meniscus is about 1.7 times higher for the oxidized protein compared to the native. Consequently, assuming the

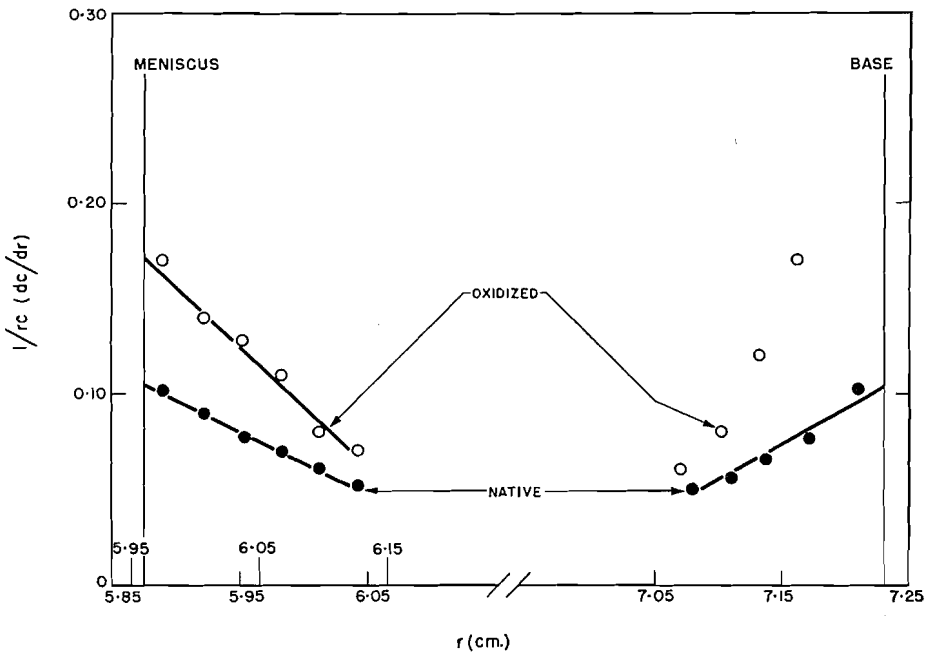

FIG. 6. Archibald's approach to sedimentation equilibrium with oxidized and native lysozyme in formamide.

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same partial specific volume for both proteins, the data indicate a molecular weight about 1.7 times that of the native for the oxidized protein. The values of δ at the base of the cell indicate monodispersity of the native sample and extensive aggregation in the oxidized sample. Similar results were obtained with globin (27) which contains 5 tryptophane residues per 68,000 gm. (36) but the extent of aggregation in the oxidized sample was much smaller than in lysozyme. This evidence together with the absence of additional α-amino terminal groups in oxidized B.P.A. strongly indicates that no scission of the polypeptide chain(s) occurred.

DISCUSSION

We tentatively assume, on the basis of the foregoing evidence, that no splitting of the polypeptide chains takes place during oxidation. Then the lower molecular weight of oxidized B.P.A., compared to that for the native albumin, indicates that previous suggestions that this protein consists of a single chain (19, 37) must be reconsidered. The earlier conclusions were based on either an assumption of fully accessible, completely unsubstituted terminal groups or the assumption of a Staudinger viscosity coefficient unmodified by the oxidation procedure. In the light of later work (7, 12, 28), it would not be surprising if either or both assumptions were invalid.

The electrophoretic patterns over a wide range of pH show that the polypeptide chains of oxidized B.P.A. are similar in charge density and therefore probably in amino acid composition. In addition, the single peak in the sedimentation patterns as well as the single maximum in the distribution function of sedimentation coefficients of oxidized B.P.A. indicates that the chains of native B.P.A. are approximately equal in weight. If the chains are similar in size, the discrepancy between the weight average and number average molecular weights of oxidized B.P.A. may be explained by interactions between the chains to produce a small proportion of aggregates of varying degrees of stability. Attractive forces, favoring formation of such aggregates, are shown by the difficulty of dissolving the material in water and by the zero value for the second virial coefficient in light-scattering experiments in water at pH 7.4, in spite of the high negative charge carried by the chains (15). Most of the aggregates are in rapid equilibrium with the smaller subunits, as shown by the single peak in sedimentation velocity experiments, and cause only a spreading of the boundary (2). However, the difference between the molecular weights at the meniscus and the base of the cell in the approach to sedimentation equilibrium shows that dissociation of a fraction of these aggregates is very slow, probably because of mechanical entanglement of the random coils. Thus the molecular weight at the meniscus in sedimentation equilibrium deviates only slightly from the light-scattering value, while at the base the weight average molecular weight increases with time.

Assuming therefore a molecular weight of 66,000 for native B.P.A. (15, 18) which contains polypeptide chains of equal size, the observed number average molecular weight shows that there are three or four such chains per molecule. However, four chains is the more probable figure because aggregation of

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components would tend to raise the estimated number average molecular weight of the oxidized material. A larger number of chains is excluded because no diffusion of protein through the osmometer membranes could be detected after seven days, although ribonuclease (mol. wt. 13,000) (32) passed through fairly rapidly under the same conditions.

The chains are presumably held together by some of the 14 disulphide bridges in B.P.A. (36) but no information is yet available on their number and location. Furthermore, because Van Vunakis and Brand found only one N-terminal amino acid residue per molecule (37), the results indicate that the other three chain ends are either substituted or inaccessible to reaction with dinitrofluorobenzene under the conditions employed.

The foregoing conclusions rest on the assumption that no polypeptide bonds were broken by performic acid oxidation. Presently available evidence for this assumption is substantial but does not exclude the possibility that tryptophane residues in a polypeptide chain may be particularly labile when linked to specific amino acids. A general investigation of the possibility is desirable.

ACKNOWLEDGMENTS

The authors should like to thank their colleagues Dr. P. A. Charlwood and D. B. Smith for discussions, advice, and criticism at all stages of the study. They are also particularly indebted to Prof. J. T. Edsall of Harvard University, and Dr. W. H. Cook, Director of the Division of Applied Biology, for stimulating advice and criticism of the methods and manuscript.

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THE VIBRATIONAL SPECTRA OF THE FORMATE, ACETATE, AND OXALATE IONS[1]

By K. Ito[2] and H. J. Bernstein

ABSTRACT

The infrared spectra of the formate, acetate, and oxalate ions have been obtained for both the solid and aqueous solution. The Raman spectra of these ions with depolarization ratios have been obtained in aqueous solution. Vibrational assignments have been made which differ slightly for the acetate ion and more markedly for the oxalate ion from earlier work. The depolarization ratios confirm Fonteyne's assignment for the formate ion.

INTRODUCTION

The Raman spectra of aqueous solutions of formate (4, 7), acetate (16), and oxalate (5, 8, 11) ions, and the infrared spectra of solid metal-formate (3), -acetate (10), and -oxalate (2) have been studied in the past but no reliable assignment has been made for the oxalate ion and in some respects the rather complete assignments for CH_3COONa and CD_3COONa in the solid state (10) and that for the formate ion merit reinvestigation.

Infrared spectra of solid sodium formate, light and heavy sodium acetate, and sodium oxalate, and their saturated solutions in H_2O and D_2O were obtained from 3–35μ. The Raman spectra of the aqueous solutions with depolarization ratios were also obtained. From these more complete vibrational data and comparison of spectra with the isoelectronic molecules nitromethane and nitrogen tetroxide vibrational assignments have been made for acetate and oxalate ions. The depolarization ratios for the Raman bands of the formate ion confirmed the assignment of Fonteyne (7).

EXPERIMENTAL

The infrared spectra were obtained with a Perkin-Elmer Model 12C double pass spectrometer with CsBr, NaCl, and LiF optics. The Raman spectra were photoelectrically recorded on a White Raman spectrometer (18) and depolarization ratios measured by comparing Raman spectra obtained with polaroid film wrapped round the sample tube first with its axis in a direction parallel to the sample tube and then perpendicular to it (6). These ratios were corrected for convergence error in a manner previously described (1, 14).

The reported infrared spectra of the aqueous solutions are not as complete as those for the solids because of the strong H_2O and D_2O absorption. The solid infrared spectra were taken of films deposited from H_2O or CH_3OH on AgCl plates or polystyrene film. Raman spectra were obtained for the saturated aqueous solutions only and the depolarization ratios of all fundamentals measured.

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[2]*National Research Laboratories Postdoctorate Research Fellow 1954–55.*

We are indebted to Dr. L. C. Leitch for the sample of CD_3COONa. All other compounds were c.p. grade.

Acetate Ion

The Raman spectrum of a saturated solution of CH_3COONa in H_2O is shown in Fig. 1 and the Raman data for solutions of CH_3COONa and CD_3COONa given in Table I.

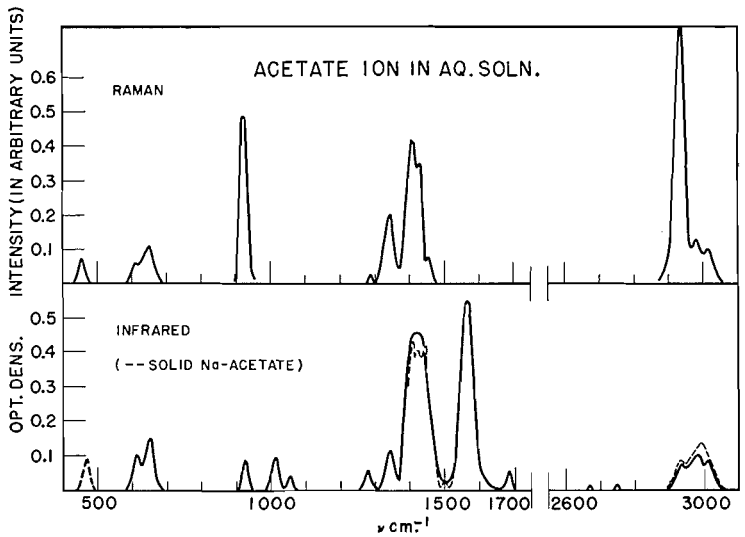

FIG. 1. The Raman and infrared spectra of the acetate ion.

TABLE I

RAMAN SPECTRA OF CH_3COONa AND CD_3COONa IN H_2O

CH_3COO^-		CD_3COO^-	
ν(cm.$^{-1}$)	ρ	ν(cm.$^{-1}$)[a]	ρ
3013	0.8_0 (D)	2264 (3.2)	0.7_4 (D)
2980	0.8_0 (D)	2231 (4.2)	0.7_4 (D)
2933	0.1_2 (P)	2185[b] (6.4)	0.1_6 (P)
1456	D	2111 (10.0)	0.08 (P)
1429	D (?)	2068[c] (2.3)	0.08 (P)
1414	0.4_9 (P)	1545 (0.61)	0.8_0 (D)
1344	0.5_6 (P)	1457[d] (0.50)	0.5_7 (P)
1289	—	1432[e] (1.5)	0.8_0 (D)
927	0.2_0 (P)	1405 (8.1)	0.3_6 (P)
649	0.5 (P)	1085 (3.6)	0.1_7 (P)
621	0.8_0 (D)	1049 (0.98)	0.8_0 (D)
471	D	1031 (8.6)	0.7_1 (D)
		883 (4.8)	0.1_2 (P)
		832 (0.61)	0.6_3 (D?)
		619 (2.6)	0.3_6 (P)
		526 (0.68)	0.7_1 (D)
		419 (0.61)	0.8_0 (D)

[a] *Values in brackets are the relative intensities referred to the 2111 cm.$^{-1}$ band.*

[b,c,d,e] *Combination bands explained as* $2\nu_2 = 2170$ (A_1), $2\nu_{13} = 2062$ (A_1), $\nu_{14}+\nu_{15} = 1466$ (A_1), *or* $\nu_9+\nu_{11} = 1466$ (A_1) *and* $\nu_5+\nu_{10} = 1451$ (B_1), *respectively (see Table II).*

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The infrared spectrum of the saturated solution of CH_3COONa in H_2O and D_2O is shown also in Fig. 1. Only the part of the spectrum of the solid that differs sensibly from that of the solution is shown in Fig. 1. The band at 480 cm.$^{-1}$ in the spectrum of the solid is not found in solution because of the strong water absorption in this region. The spectrum of the solid agrees with that found by Jones and McLaren (10) and the band positions have been used in Table II in the column giving their assignment. The infrared spectrum of solid CD_3COONa is the same as that previously reported (10), and bands were observed at 2267 (m), 2288 (w), 1546 (s), 1408 (s), 1084 (w), 1043 (w), 940 (m), 883 (w), and 833 (m) cm.$^{-1}$ in the infrared spectrum of CD_3COONa in H_2O. In Table II the assignment for CH_3COO^- (solid) by Jones and McLaren

TABLE II

VIBRATIONAL ASSIGNMENT OF THE ACETATE ION

C_{2v}	$\left(\begin{matrix}O\\O\end{matrix}\!\!>\!C\!-\!CH_3\right)^-$	CH_3COO^- (solid)[a] Jones, McLaren	CH_3COO^- (solution) This work	CH_3NO_2 (gas) Wells, Wilson	CD_3COO^- (solution) This work	Teller–Redlich product rule ratios	
						Obs.	Theor.
a_1 ν_1	C—H stretching	2936	2935 (P)	2965	2111 (P)		
ν_2	CH_3 deformation	1430	1344 (P)	1413	1085 (P)		
ν_3	C—O stretching	1414	1413 (P)	1384	1406 (P)	1.91	1.95
ν_4	C—C stretching	924	926 (P)	921	883 (P)		
ν_5	COO deformation	646	650 (P)	647	619 (P)		
a_2 ν_6	Torsion	—	—	—	—		
b_1 ν_7	C—H stretching	2989	3010 (D) or 2981 (D)	3048	2264 (D) or 2231 (D)		
ν_8	C—O stretching	1578	1556	1582	1545 (D)		
ν_9	CH_3 deformation	1443	1429 (D)	1449	1047 (D)	2.53	2.58
ν_{10}	CH_3 rocking	1009	1020	1097	832 (D?)		
ν_{11}	COO rocking (in-plane)	460	471 (D)	476	419 (D)		
b_2 ν_{12}	C—H stretching	2989	2981 (D) or 3010 (D)	3048	2231 (D) or 2264 (D)		
ν_{13}	CH_3 deformation	1498	1456 (D)	1488	1031 (D)	2.49	2.53
ν_{14}	CH_3 rocking	1042	1052	1153	940		
ν_{15}	COO rocking (out-of-plane)	615	621 (D)	599	526 (D)		

[a] *In this assignment the frequencies measured here have been used.*

(but using our measured frequencies), that for CH_3NO_2 by Wells and Wilson (17), and the present assignments for CH_3COO^- and CD_3COO^- are given. The assignments are based on C_{2v} point group symmetry (17). The new information provided by the above spectra and comparison with the fundamentals of the isoelectronic CH_3NO_2 molecule have been the basis for the present assignment and as can be seen from Table II it differs from that of Jones and McLaren for CH_3COO^- in several respects. In particular, ν_2, the fairly strong polarized Raman band at 1344 cm.$^{-1}$, is taken as a fundamental here instead of the rather weak infrared band at 1498 cm.$^{-1}$ which is not observed in the Raman spectrum. This band at 1498 cm.$^{-1}$ is then to be interpreted as a difference tone (see Table III). The present assignments for ν_2 and ν_3 were confirmed from the depolarization ratios and comparison of the Raman spectra of CH_3COO^- and CD_3COO^-. Other changes are to assign the band at 1429 cm.$^{-1}$, which is found to be depolarized, as ν_9 and the band at 1443 cm.$^{-1}$ in the infrared spectrum of the solid as ν_{13}. One other small

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modification is introduced by the fact that three bands in the CH stretching region are observed in the infrared and Raman spectra of the solution whereas there are only two in the infrared spectrum of the solid (see Fig. 1). Assuming all three to be fundamentals, ν_1 is readily assigned because of its depolarization ratio but a choice is left for ν_7 and ν_{12} as indicated in Table II.

Of the two COO rocking modes ν_{11} and ν_{15} the higher was taken as the out-of-plane mode ν_{15}, since it was expected that the π electron cloud in the COO^- group accumulating in the direction perpendicular to the COO^- plane gives rise to more repulsion in the potential energy function for the out-of-plane mode than for the in-plane mode. The moment of inertia argument used by Wells and Wilson for the corresponding assignment in CH_3NO_2 leads to this result also (which was recognized also by Jones and McLaren in their assignment).

Our assignment for CD_3COO^- is essentially the same as that reported by Jones and McLaren except for the CD stretching modes. From Raman spectrum and depolarization ratios (see Table I) the band at 2231 $cm.^{-1}$

TABLE III

COMBINATION AND DIFFERENCE FREQUENCIES FOR INFRARED BANDS OF CH_3COO^-

Aqueous solution		Solid (Na salt)		Assignment	Irred. representation
Obs.	Calc.	Obs.	Calc.		
2746	2757	2740	2752	$\nu_2+\nu_3$	A_1
2668	2688	2653	2676	$2\times\nu_2$	A_1
2583	2576	2605	2587	$\nu_8+\nu_{10}$	A_1
		2557	2550	$\nu_7-\nu_{11}$	A_1
2486	2482	2495	2499	$\nu_8+\nu_4$	B_1
2416	2433	2424	2423	$\nu_3+\nu_{10}$	B_1
1911	1915		1927	$\nu_1-\nu_{10}$	B_1
1693	1702		1688	$\nu_5+\nu_{14}$	B_2
		1498	1506	$\nu_1-\nu_2$	A_1
			1493	$\nu_1-\nu_9$	B_1
1289*	1300	1300	1292	$2\times\nu_5$	A_1
1277	1271	1254	1261	$\nu_5+\nu_{15}$	B_2

Observed in the Raman spectrum.

assigned by the above authors to ν_1 must be either ν_7 or ν_{12}. In Table III the combination bands for CH_3COO^- observed in the infrared spectrum are given with plausible assignments.

The present assignments for light and heavy acetate ion (solution) are consistent with the product rule as shown in the last column of Table II. The theoretical ratios are taken from the paper of Jones and McLaren (10) which were calculated using dimensions of the solid ion. Since these ratios are very insensitive to small changes in molecular dimensions they will be very nearly the same for the solid ion and the ion in solution.

Oxalate Ion

The Raman spectrum of a saturated solution of potassium oxalate in H_2O is shown in Fig. 2 and the Raman data given in Table IV. The infrared spectrum of saturated solutions of potassium and cesium oxalate in H_2O

and D_2O is shown also in Fig. 2. The frequencies of the fundamentals are given in Table IV and those of the combination bands in Table V. The infrared spectrum of solid sodium oxalate is listed in Table IV (fundamentals) and

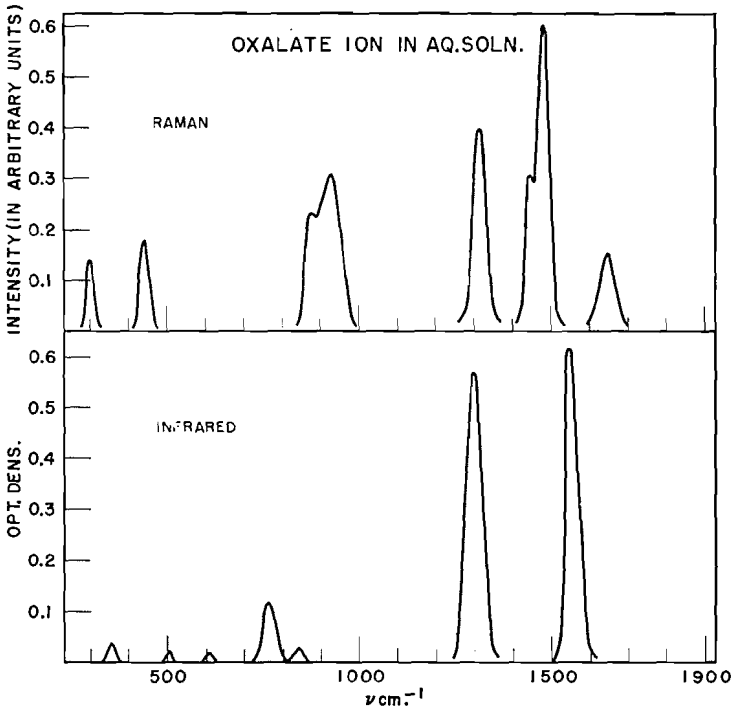

FIG. 2. The Raman and infrared spectra of the oxalate ion.

Table V (combination tones). The principal difference between the solid and solution infrared spectra is that the band at 507 cm.$^{-1}$ in the solid is by

TABLE IV

VIBRATIONAL ASSIGNMENT OF THE OXALATE ION

Irred. rep. (D_{2h})	$\left(\begin{smallmatrix} O & & O \\ & C-C & \\ O & & O \end{smallmatrix}\right)^{--}$	$C_2O_4^{--}$ Solid Na salt	$C_2O_4^{--}$ Aq. soln.	$C_2O_4^{--}$ Dep. ratio	N_2O_4 gas	Previous assignment for $C_2O_4^{--}$ by Lecomte *et al.*	
a_{1g}	ν_1 C—O stretching		1488	0.3_4 (P)	1360	$\sim$ 1480	Raman active
	ν_2 COO deformation		904	0.1_9 (P)	813	$\sim$ 900	
	ν_3 C—C stretching		445	0.5_9 (P)	283	$\sim$ 320	
b_{1g}	ν_4 C—O stretching		1660	0.8_6 (D)	1724	$\sim$ 1640	
	ν_5 COO rocking (in-plane)		300	0.8_5 (D)	500	525–575	
b_{2g}	ν_6 COO rocking (out-of-plane)		1305	0.8_2 (D)	(1480)	$\sim$ 450	
a_{1u}	ν_7 Torsion		—		—		
b_{1u}	ν_8 COO rocking (out-of-plane)	507	500		(680)	665	Infrared active
b_{2u}	ν_9 C—O stretching	1640* 1405	1555		1749	1500–1600	
	ν_{10} COO rocking (in-plane)		(160)		380	$\sim$ 370	
b_{3u}	ν_{11} C—O stretching	1319	1300		1265	1200–1300	
	ν_{12} COO deformation	766	766		752	750–800	

**Split by the Fermi resonance into two bands with equal intensity.*

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far the strongest band in this region, whereas in solution it is weak (at 500 cm.$^{-1}$) and comparable in intensity to the bands at 361 and 605 cm.$^{-1}$. Because of its strong absorption in the solid this band was chosen as a fundamental. Another feature in the infrared spectrum of the solid is the doublet

TABLE V

COMBINATION AND DIFFERENCE FREQUENCIES FOR THE INFRARED BANDS OF $C_2O_4^{--}$

Aqueous solution		Solid Na salt,	Assignment	Irred.
Obs.	Calc.	obs.		rep.
		3134		
		3054		
	2960	2935	$\nu_4+\nu_{11}$	B_{2u}
2860		2862	?	
2782	2788	2767	$\nu_1+\nu_{11}$	B_{3u}
2604	2605		$\nu_6+\nu_{11}$	B_{1u}
2474		2479	?	
		1885	?	
1452*	1460		$\nu_{10}+\nu_{11}$	B_{1g}
	1255	1249	$\nu_9-\nu_5$	B_{3u}
		1029	?	
	894	898	$\nu_4-\nu_{12}$	B_{2u}
		873	?	
888*	890		$2\nu_3$	A_{1g}
846	855	854	$\nu_{11}-\nu_3$	B_{3u}
605	605	611	$\nu_3+\nu_{10}$	B_{2u}
	539	533	$\nu_6-\nu_{12}$	B_{1u}
361	360	363	$\nu_4-\nu_{11}$	B_{3u}

**Observed in the Raman spectrum.*

1405 and 1640 cm.$^{-1}$ which may be explained on the basis of Fermi resonance of ν_9 (b_{2u}) with $\nu_{11}+\nu_5$ (B_{2u}). In solution, only one strong band at 1555 cm.$^{-1}$ is observed. The oxalate ion has D_{2h} symmetry in the solid sodium salt (9) and is assumed to have the same symmetry in solution. This is borne out by the infrared and Raman spectra which exhibit the character of mutual exclusion. In Table IV the assignment for $C_2O_4^{--}$ is given for the solid and solution made on the basis of the selection rules, depolarization ratios, and comparison with the spectrum of isoelectronic N_2O_4 (15). In the last column of the table the previous assignment of Lecomte *et al.* (2) is given for comparison. Since our infrared investigation covered a larger region than that investigated previously (2) and since our depolarization data are more complete than those of an earlier investigation (8), several differences between the present and the earlier (2) assignments are not unexpected. In particular the depolarization ratio of the band at 445 cm.$^{-1}$ established it as ν_3. By analogy with N_2O_4 the other low lying Raman band is ν_5 and the high one at 1305 cm.$^{-1}$ is then ν_6. The band at 665 cm.$^{-1}$ reported by Lecomte *et al.* (2) occurring in the region of CO_2 absorption was not observed here. As ν_8 we choose the strong infrared band (solid) at 507 cm^{-1}. The ν_{10} mode was calculated here as ~160 cm.$^{-1}$ and estimated previously (2) to be ~370 cm^{-1}. The calculation for ν_{10} follows from the Urey Bradley treatment by Shimanouchi *et al.* (12) for D_{2h} molecules. Here it was shown that the ratio of the product of the two b_{1g} frequencies to

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that of the two b_{2u} frequencies is a function of masses and geometry only and independent of force constants if the interaction between COO groups on different C atoms is neglected. The structural parameters used to calculate this ratio are given below (9):

$$r_{CC} = 1.56\,\text{Å},\ r_{CO} = 1.24\,\text{Å},\ \angle OCO = 125°.$$

The value of $\nu_{10} = 160$ cm.$^{-1}$ is further supported by the assignment of two observed combination tones at 1452 cm.$^{-1}$ in the Raman spectrum and 605 cm.$^{-1}$ (solution), 611 cm.$^{-1}$ (solid) in the infrared spectrum. Other interpretations of these bands are not readily forthcoming.

In Table V the combination bands observed in the infrared spectrum are listed with plausible assignments. The bands at 2862, 2479, 1885, 1029, and 873 cm.$^{-1}$ in the infrared spectrum of the solid cannot be interpreted in terms of binary combinations of the listed fundamentals.

Formate Ion

The Raman spectrum of a saturated solution of potassium or sodium formate in H_2O is shown in Fig. 3 and the frequencies and depolarization ratios

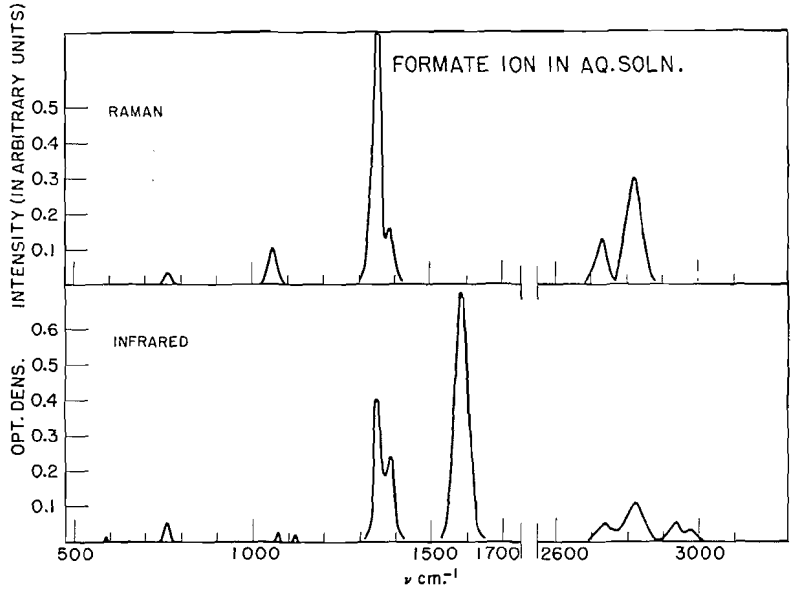

FIG. 3. The Raman and infrared spectra of the formate ion.

given in Table VI. The infrared spectrum of a saturated solution of these salts in H_2O and D_2O is given also in Fig. 3 and the frequencies in Table VI (fundamentals) and Table VII (combination tones). The infrared spectrum of solid sodium formate is given in Table VI (fundamentals) and in Table VII (combination tones).

The present assignment for the formate ion made on the basis of C_{2v} symmetry and the measured depolarization ratios is given in Table VI.

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Of the two rocking frequencies, ν_5 and ν_6, the higher one might be expected to be the out-of-plane mode analogous to the acetate and oxalate ions but these were assigned as shown in the table because of the results of Newman (13) obtained from the polarized infrared spectra of solid sodium formate. The present assignment for the aqueous solution is the same as that by

TABLE VI

VIBRATIONAL ASSIGNMENT OF THE FOMATE ION

Irred. reptn.		$\left(\begin{matrix}O\\O\end{matrix}\!\!>\!C\!-\!H\right)^-$	Raman $\Delta\nu$	Infrared			
				Dep. ratio (aq. soln. of K salt)	ν (aq. soln. of K salt)	ν (solid Na salt) This work	ν (solid Na salt) Newman
a_1	ν_1	C—H stretching	2803	0.37 (P)	2803	2841	2870
	ν_2	C—O stretching	1349	0.29 (P)	1351	1366	1377
	ν_3	COO deformation	762	0.43 (P)	760	772	784
b_1	ν_4	C—O stretching			1585	1567	1620
	ν_5	COO rocking (C—H bending, in-plane)	1380	0.89 (D)	1383	1377	1365
b_2	ν_6	COO rocking (C—H bending, out-of-plane)	1066	0.83 (D)	1069	1073	1070

Fonteyne (7) which was made on the basis of the Raman spectrum of the light and heavy formate ion in aqueous solution without measuring the depolarization ratios. Newman's assignments (last column of Table VI) of

TABLE VII

COMBINATION AND DIFFERENCE FREQUENCIES FOR THE INFRARED BANDS OF $HCOO^-$

Aqueous solution				Solid (Na salt)		
Obs.	Calc.	Assignment	Irred. rep.	Obs.	Calc.	Assignment
				4313	4319	$2953+\nu_2$
4180	4186	$\nu_1+\nu_5$	B_1	4200	4218	$\nu_1+\nu_5$
4091	4111	$2728+\nu_5$	A_1	4085	4097	$2720+\nu_5$
				3611	3613	$\nu_1+\nu_3$
3181	3178	$2\nu_4$	A_1	3190	3194	$2\nu_4+60$
				3070	3074	$2\nu_4-60$
2974	2972	$\nu_4+\nu_5$	A_1	2953	2944	$\nu_4+\nu_5$
				2791	2781	ν_1-60
2728	2734	$\nu_2+\nu_5$	B_1	2720	2743	$\nu_2+\nu_5$
				2599	2600	$2720-2\times60$
2415	2420	$\nu_2+\nu_6$	B_2	2435	2439	$\nu_2+\nu_6$
				2134	2138	$\nu_2+\nu_3$
				1700	1707	ν_4+140
				1620	1627	ν_4+60
				1514	1517	ν_5+140
				1226	1237	ν_5-140
				1013	1013	ν_6-60
				958	953	$\nu_6-2\times60$
				923	930	ν_6-140
				898	892	$\nu_3+2\times60$
				840	832	ν_3+60

the a_1 C—O stretching and the b_1 COO rocking were reversed as shown in the seventh column of Table VI because of the analogy with the corresponding fundamentals in the aqueous solution.

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The infrared spectra of solid sodium formate were obtained of the solid films deposited from H_2O, a mixture of H_2O and CH_3OH, or a mixture of H_2O and acetone, on AgCl and NaCl plates. All solid samples were dried over P_2O_5 in a desiccator and had no absorption band in the O—H stretching region, 3100–3800 cm.$^{-1}$, showing that the samples were indeed anhydrous. The infrared spectra of these samples seemed to change slightly from sample to sample depending on the method of preparation, in contrast to the infrared spectra of the acetate and oxalate salts. In particular the b_1 C—O stretching mode shows a rather complicated behavior and has two bands at 1567 cm.$^{-1}$ and 1514 cm.$^{-1}$ in some samples. The intensity of the latter band was increased by dehydration in a desiccator and was even stronger in some cases than that at higher wave numbers. However, the band at 1567 cm.$^{-1}$ was assigned as a fundamental by analogy with the fundamentals for the aqueous solution. The band at 1620 cm.$^{-1}$ which was assigned as a fundamental by Newman was observed only in some samples as a weak band or a small shoulder.

Table VII shows the combination and difference bands observed in the infrared spectrum and a possible assignment. In the case of the infrared spectrum of the solid, it is necessary to assume lattice vibrational modes coupling with the internal vibrational modes of the formate ion in order to explain the observed combination bands satisfactorily. Two lattice frequencies at 140 cm.$^{-1}$ and 60 cm.$^{-1}$ have been assumed in the seventh column of Table VII which are used to interpret 13 of the 21 combination tones. There are several possible choices of the assignments for some bands in the solid infrared spectrum but only one is shown rather arbitrarily.

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NOTES

SYNTHESIS OF METHYL-d_3 FORMATE*

By R. Renaud and L. C. Leitch

In earlier papers of this series (1, 2) Nolin reported the preparation of several deuterated methyl and ethyl acetates from the alkyl iodides and silver acetate. On account of the instability of silver formate the method is not directly applicable to the synthesis of methyl-d_3 formate. This ester has now been prepared in moderately good yields by the acid-catalyzed transesterification of methyl-d_3 butyrate and *n*-butyl formate:

$$C_3H_7CO_2CD_3 + HCO_2C_4H_9 \rightarrow HCO_2CD_3 + C_3H_7CO_2C_4H_9.$$

The methyl-d_3 butyrate was prepared in nearly quantitative yield from methyl-d_3 bromide and silver butyrate. The methyl-d_3 bromide was in turn prepared by the brominative decarboxylation of silver acetate-d_3 in carbon tetrachloride as described in the experimental part rather than by the method reported in reference (3).

It is of interest to compare the mass spectra of methyl and methyl-d_3 formates:

$HCOOCH_3$		$HCOOCD_3$	
60	100	63	100.0
59	1.86	62	4.56
		61	0.1

Since the intensity of the 61 peak—due to loss of D—is so small in methyl-d_3 formate the peaks at 59 in the spectrum of methyl formate and 62 in the spectrum of methyl-d_3 formate must be due to loss of H in the formoxy group rather than in the methyl group.

EXPERIMENTAL

Silver Butyrate

Silver butyrate was prepared by adding a solution of 77 gm. of silver nitrate in 400 ml. of water in small portions to a stirred solution of 40 gm. of *n*-butyric acid in 200 ml. of water containing sufficient aqueous ammonia for neutralization. The salt was recrystallized from boiling water, dried for a day over phosphorus pentoxide in a vacuum desiccator, and stored in an amber bottle. The yield was nearly theoretical.

Methyl-d_3 Bromide

Silver acetate-d_3 (34.0 gm., 0.2 mole) was placed in a 500 ml. four-necked round-bottomed flask equipped with a funnel, a thermometer, a mechanical

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stirrer with a graphite packed gland, and a reflux condenser. Three spiral traps, two of which were cooled in dry ice and carbon dioxide at −78° and the third at −30°C., were connected to the outlet of the condenser. A solution of 11 ml. of dry bromine in 75 ml. of dry carbon tetrachloride was added to the stirred silver salt at the rate of about a drop every two seconds. The temperature of the reaction mixture was kept at 27–30°. Addition of the bromine required about four hours. The reaction mixture was then slowly heated to the boiling point and refluxed from one to one and one-half hours while a current of dry nitrogen was passed in. The contents of the first trap were then distilled into the second. The third trap was generally empty. The crude product was distilled on the vacuum line through ascarite to remove dissolved carbon dioxide and bromine. The distillate was redistilled twice from a bath at −40°C. into a trap cooled in liquid nitrogen. The weight of crude methyl-d_3 bromide was 19.0 gm. After another distillation from a trap at −78° the vapor pressure of the product at 0° was 679 mm. There was little change in the vapor pressure of various fractions distilled at 0°C. The yield was 17.5 gm. (89.3% of the theoretical amount). Mass analysis showed a purity of 97.8 mol. % CD_3Br or 99.2 atom % D.

Methyl-d_3 Butyrate

Silver butyrate (8.3 gm., 0.04 mole) was heated with 4.1 gm. (0.04 mole) of methyl-d_3 bromide in a sealed tube for 16 hr. at 80°C. in a rocking furnace. The methyl-d_3 butyrate was isolated by attaching the opened tube to a Stock trap cooled in liquid nitrogen on a vacuum manifold and evacuating to a pressure of 0.1 mm. The yield of ester recovered in the trap, n_D^{20} 1.3879, vapor pressure 30 mm. at 22°C., was quantitative. Methyl butyrate prepared in the same way had n_D^{20} 1.3874.

Methyl-d_3 Formate

A mixture of 4.5 gm. of *n*-butyl formate, 4.1 gm. of methyl-d_3 butyrate, and three drops of concentrated sulphuric acid was distilled in a column packed with glass helices. The yield of methyl-d_3 formate, b.p. 31–32°C., n_D^{20} 1.3431, was 1.5 gm. (61% of the theoretical). Its mass spectrum gave a deuterium content of 97.6 mol. % or 99.07 at. %.

ACKNOWLEDGMENTS

The authors are indebted to Miss F. Gauthier and Dr. F. P. Lossing for the mass analyses.

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SYNTHESIS OF DEUTERATED DIMETHYL CARBONATE*

By R. Renaud and L. C. Leitch

The well-known synthesis of alkyl carbonates from phosgene and alcohols is not suitable for the preparation of deuterated dimethyl carbonate because methyl-d_3 alcohol is not readily available. Since methyl-d_3 bromide is now easily obtained by a method reported previously by one of us (2) it seemed worth while to attempt the preparation of dimethyl carbonate from methyl bromide and silver carbonate. Diethyl carbonate labelled with C^{14} was recently prepared by Eisenhauer, Pepper, Jaques, and Spinks (1) by refluxing a suspension of silver carbonate-C^{14}, ethyl iodide, and triethylamine under nitrogen. In the present work it was found that no reaction took place when methyl iodide and silver carbonate were heated under reflux for a day. However, when these reactants were treated for 65 hr. in a sealed tube at 60°, a 75% yield of dimethyl carbonate was obtained. With methyl bromide the yield was nearly quantitative, possibly because the product was more easily separated from unchanged methyl bromide. Similar results were obtained when methyl-d_3 bromide was employed. Dehalogenation of hexachloromethyl carbonate with zinc dust and acetic acid did not give the desired product. Evolution of carbon dioxide took place presumably because of hydrolysis of the ester and no dimethyl carbonate could be isolated.

EXPERIMENTAL

Dimethyl Carbonate

(*a*) *From Methyl Iodide and Silver Carbonate*

Methyl iodide (14.7 gm., 0.11 mole) was distilled on a vacuum manifold into a tube containing 13.8 gm. (0.05 mole) of dry silver carbonate. The tube was sealed and heated in a rocking furnace at 60°C. for 65 hr. The liquid phase was distilled off on a vacuum line into a distilling flask. Fractional distillation of the distillate through a small column packed with glass helices afforded a 75% yield of dimethyl carbonate, b.p. 89–91°C., n_D^{20} 1.3694.

(*b*) *From Methyl Bromide and Silver Carbonate*

A similar experiment with methyl bromide gave a nearly quantitative yield of dimethyl carbonate. An attempt to shorten the reaction time by raising the temperature to 90°C. resulted in decomposition of the silver carbonate with evolution of carbon dioxide.

Dimethyl-d_3 Carbonate

A mixture of 5.6 ml. (10.0 gm., 0.12 mole) of methyl-d_3 bromide prepared as described in reference (2) and 13.8 gm. of silver carbonate was heated for 65 hr. at 60°C. The reaction product was isolated and purified as already described. The yield of deuterated dimethyl carbonate, b.p. 89–90°C., n_D^{20}

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ACKNOWLEDGMENTS

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CHOLESTEROL FROM ASCARIS LUMBRICOIDES (NEMATODA)*

BY DONALD FAIRBAIRN AND R. NORMAN JONES

Conclusive evidence for the existence of sterols in any species belonging to the phylum Nematoda was not available until it was shown (1) that the reproductive organs of the common pig roundworm, *Ascaris lumbricoides*, contain small amounts of a mixture of saturated and unsaturated sterols in the approximate ratio 1:3. Although infrared analysis of the mixed sterol acetates suggested that cholesterol might be one component of the mixture, insufficient material was available for positive identification.

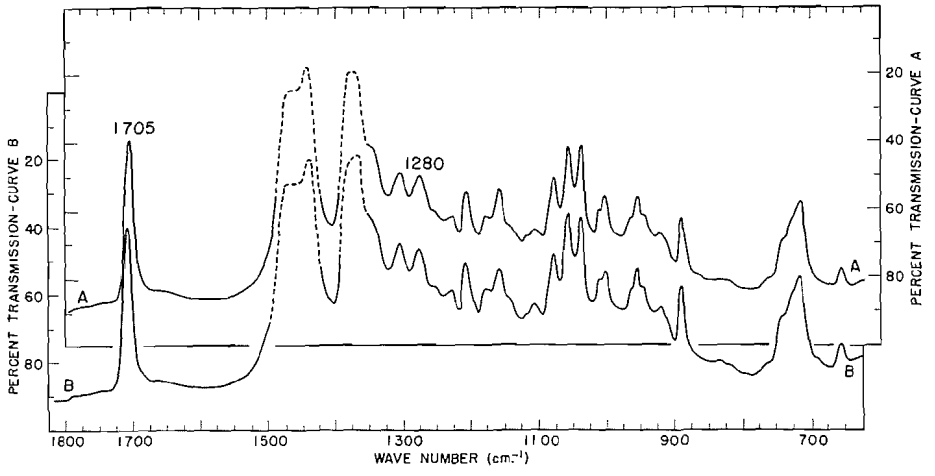

FIG. 1. Curve A. Infrared spectrum of sample of cholesterol dibromide prepared concurrently with ascaris sterol dibromide.
Curve B. Infrared spectrum of ascaris sterol dibromide. (Nujol mulls. - - -region of Nujol absorption.)

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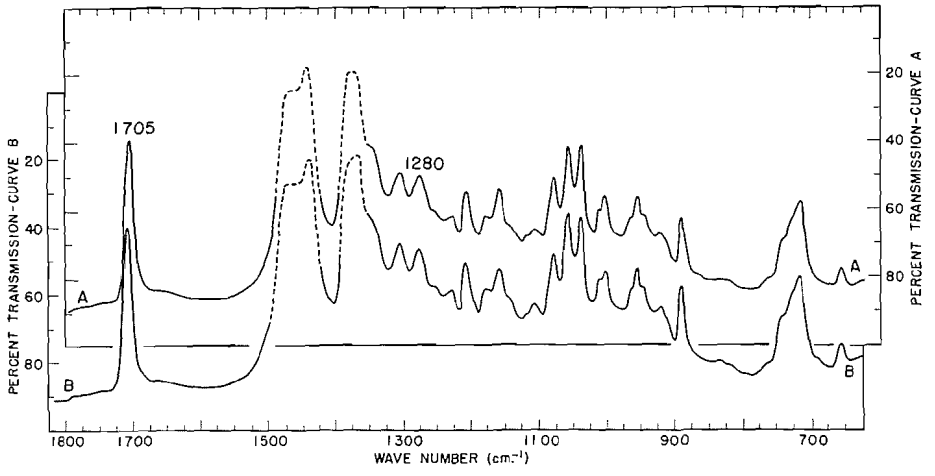

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An extension of the investigation has resulted in the isolation and identification of cholesterol as the dibromide. From the total lipids extracted from the blended muscle and reproductive tissues of mature female parasites, total sterols were precipitated as the digitonides and subsequently recovered in the free form (4). The recrystallized mixture was then brominated (3), insoluble bromides separated, and saturated sterols isolated as the digitonides. Recrystallization of the bromide from ether and glacial acetic acid yielded a product identical in melting point and mixed melting point with cholesterol dibromide. The saturated sterol(s) has not yet been identified.

The infrared spectra of the ascaris sterol dibromide and a sample of cholesterol dibromide prepared concurrently are shown in Curves A and B of Fig. 1. The similarity of these curves confirms the identification of the ascaris sterol, but both curves show absorption at 1705 and 1280 cm.$^{-1}$ which is not present in Fig. 2, obtained from a second sample of cholesterol dibromide immediately following crystallization from ethyl acetate – methanol at room temperature.* This difference is attributed to the partial photolysis or autoxidation of the first two samples during transshipment prior to analysis.

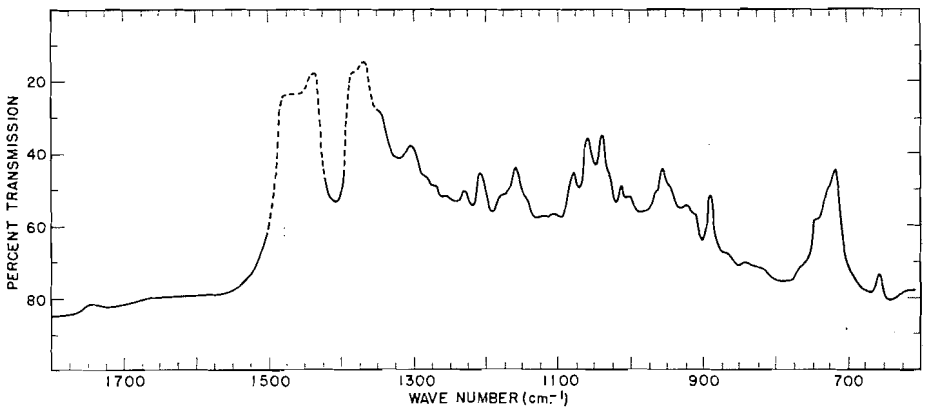

FIG. 2. Infrared spectrum of freshly prepared cholesterol 5α,6β-dibromide.

The bromination method employed resulted in characteristically low yields of ascaris sterol bromide, which were necessarily accepted because it was desirable to isolate saturated sterols quantitatively from the mother liquor. For this reason the identification of cholesterol as the main unsaturated sterol depended upon the provision of auxiliary evidence such as (1) the similarly low yield obtained by bromination of pure cholesterol, (2) the iodine number and rate and intensity of color development with the Schoenheimer-Sperry reagent (1, 2), and (3) the infrared spectrum of the mixed acetates (1), which resembled closely that of authentic cholesterol acetate. These observations led to the conclusion that large amounts of unsaturated sterols other than cholesterol were absent.

We wish to thank Dr. A. Nickon for the preparation of this material.

EXPERIMENTAL

Thirty grams of the fats obtained by extraction of 2 kgm. of ascaris muscle and reproductive tissue (representing 2.6 kgm. of adult female parasites) was shaken vigorously with five volumes of ethanol (twice), after which the clear solution was treated with 1% digitonin in ethanol. The sterol digitonides so obtained were washed twice by centrifugation with ethanol–ether (1:2) and three times with ether, dried, decomposed in a minimum volume of dry pyridine at 70°, and the free digitonin precipitated by addition of 10 volumes of dry, ethanol-free ether. The supernatant solution contained 260 mgm. of mixed sterols which were recrystallized once from 80% methanol (m.p. 123–124°). Bromination of 216 mgm. of this product provided 67 mgm. of sterol bromide (29% yield, calculated as cholesterol dibromide and including the necessary correction for saturated sterol content) which was recrystallized twice from ether and glacial acetic acid (1:3). Authentic cholesterol dibromide was prepared by the same procedure (yield, 31%). M.p. cholesterol dibromide 115.5–116°, ascaris sterol bromide 115–116°, mixed m.p. 115–116°; identical infrared spectra.

The mother liquor obtained from the bromination of ascaris sterols was treated with digitonin to remove saturated (unbrominated) sterol. From the resulting digitonide 54 mgm. of saturated sterol was recovered (iodine number, 2; m.p. 131–132°).

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OTTAWA, CANADA.

PREPARATION OF TRIBUTYL ANTIMONITE

BY L. J. CARBONNEAU AND D. C. DOWNING

There is only one reference in the literature to a direct preparation of antimony esters (2). In it, antimony trioxide was reacted with the corresponding alcohol, under water-removing conditions.

We attempted to carry out this preparation with butanol, without success. It was then found that the ester could be readily prepared, in high (86%) yield, by reacting butanol and antimony trichloride.

Into a 500 ml. three-necked flask, equipped with a mechanical stirrer, reflux condenser, thermometer, and provision for solid addition, was weighed 74.1 gm.

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Thirty grams of the fats obtained by extraction of 2 kgm. of ascaris muscle and reproductive tissue (representing 2.6 kgm. of adult female parasites) was shaken vigorously with five volumes of ethanol (twice), after which the clear solution was treated with 1% digitonin in ethanol. The sterol digitonides so obtained were washed twice by centrifugation with ethanol–ether (1:2) and three times with ether, dried, decomposed in a minimum volume of dry pyridine at 70°, and the free digitonin precipitated by addition of 10 volumes of dry, ethanol-free ether. The supernatant solution contained 260 mgm. of mixed sterols which were recrystallized once from 80% methanol (m.p. 123–124°). Bromination of 216 mgm. of this product provided 67 mgm. of sterol bromide (29% yield, calculated as cholesterol dibromide and including the necessary correction for saturated sterol content) which was recrystallized twice from ether and glacial acetic acid (1:3). Authentic cholesterol dibromide was prepared by the same procedure (yield, 31%). M.p. cholesterol dibromide 115.5–116°, ascaris sterol bromide 115–116°, mixed m.p. 115–116°; identical infrared spectra.

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Into a 500 ml. three-necked flask, equipped with a mechanical stirrer, reflux condenser, thermometer, and provision for solid addition, was weighed 74.1 gm.

(1.0 mole, Shaw. Chem. dried) *n*-butanol. With continuous stirring, 76.0 gm. (0.33 mole, Mallinckrodt A.R.) antimony trichloride was added over a 0.5 hr. period. The temperature rose from 26–30° C. No cooling was used. Stirring was continued for an additional 0.5 hr. Ammonia gas was then bubbled through the stirred mixture until no more gas was absorbed (excess ammonia coming through), using external cooling to keep the reaction below 25° C. During precipitation of ammonium chloride, 250 ml. of isoheptane was added to thin the mixture. The mixture was filtered on a Büchner funnel, and the precipitate washed with 5×50 ml. of isoheptane.

The filtrate was distilled without a column at 200 mm. up to a pot temperature of 140° C., to remove isoheptane and unreacted butanol. The pressure was then reduced to 5.5 mm. and the fraction boiling at 139–141° C., collected, 97.0 gm. (86% of theory), $n_D^{20} = 1.4792$. The previously reported boiling point is 138.5–139.5° C. at 5.5 mm. (1).

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THE CRYSTAL STRUCTURE OF DES-(OXYMETHYLENE)-LYCOCTONINE HYDRIODIDE MONOHYDRATE*

BY MARIA PRZYBYLSKA AND LÉO MARION

Des-(oxymethylene)-lycoctonine hydriodide monohydrate, $C_{24}H_{39}O_6N.HI.H_2O$, (1) crystallizes from a mixture of methanol and acetone in colorless, fine, monoclinic sphenoidal prisms, elongated along [010]. There are two optically active molecules per unit cell and since the only reflections absent are $0k0$ with k odd, the space group is $P2_1$. The unit cell dimensions are

$$a = 12.79 \text{ Å},$$
$$b = 9.44 \text{ Å},$$
$$c = 11.00 \text{ Å},$$
$$\beta = 97°45'.$$

Three-dimensional data were obtained from Weissenberg photographs and the number of reflections observed amounted to 6% of those theoretically possible. The x and z co-ordinates of the iodine atom were derived from a Patterson projection on (010).

A three-dimensional Fourier synthesis was carried out using the phases based on the iodine contributions only. By placing the iodine atom at $y = 0.250$ the elements of symmetry of space group $P2_1/m$ were introduced and the Fourier pattern showed in addition to real atoms at x, y, z, and $-x$, $\frac{1}{2}+y$,

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On this page, in line 7 up, 6% should read 68%.

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(1.0 mole, Shaw. Chem. dried) *n*-butanol. With continuous stirring, 76.0 gm. (0.33 mole, Mallinckrodt A.R.) antimony trichloride was added over a 0.5 hr. period. The temperature rose from 26–30° C. No cooling was used. Stirring was continued for an additional 0.5 hr. Ammonia gas was then bubbled through the stirred mixture until no more gas was absorbed (excess ammonia coming through), using external cooling to keep the reaction below 25° C. During precipitation of ammonium chloride, 250 ml. of isoheptane was added to thin the mixture. The mixture was filtered on a Büchner funnel, and the precipitate washed with 5×50 ml. of isoheptane.

The filtrate was distilled without a column at 200 mm. up to a pot temperature of 140° C., to remove isoheptane and unreacted butanol. The pressure was then reduced to 5.5 mm. and the fraction boiling at 139–141° C., collected, 97.0 gm. (86% of theory), $n_D^{20} = 1.4792$. The previously reported boiling point is 138.5–139.5° C. at 5.5 mm. (1).

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RECEIVED NOVEMBER 7, 1955.
RESEARCH LABORATORIES,
SHAWINIGAN CHEMICALS LIMITED,
SHAWINIGAN FALLS, QUE.

THE CRYSTAL STRUCTURE OF DES-(OXYMETHYLENE)-LYCOCTONINE HYDRIODIDE MONOHYDRATE*

BY MARIA PRZYBYLSKA AND LÉO MARION

Des-(oxymethylene)-lycoctonine hydriodide monohydrate, $C_{24}H_{39}O_6N.HI.H_2O$, (1) crystallizes from a mixture of methanol and acetone in colorless, fine, monoclinic sphenoidal prisms, elongated along [010]. There are two optically active molecules per unit cell and since the only reflections absent are $0k0$ with k odd, the space group is $P2_1$. The unit cell dimensions are

$$a = 12.79 \text{ Å},$$
$$b = 9.44 \text{ Å},$$
$$c = 11.00 \text{ Å},$$
$$\beta = 97°45'.$$

Three-dimensional data were obtained from Weissenberg photographs and the number of reflections observed amounted to 6% of those theoretically possible. The x and z co-ordinates of the iodine atom were derived from a Patterson projection on (010).

A three-dimensional Fourier synthesis was carried out using the phases based on the iodine contributions only. By placing the iodine atom at $y = 0.250$ the elements of symmetry of space group $P2_1/m$ were introduced and the Fourier pattern showed in addition to real atoms at x, y, z, and $-x$, $\frac{1}{2}+y$,

*Issued as N.R.C. No. 3842.

On this page, in line 7 up, 6% should read 68%.

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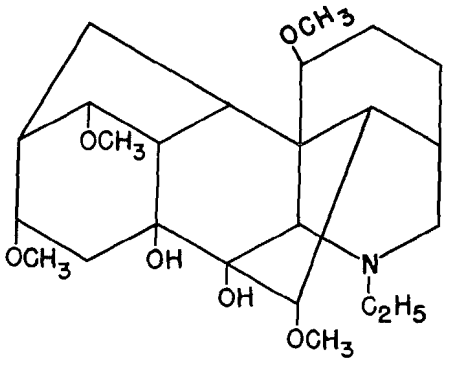
$-z$, unreal peaks at $-x$, $-y$, $-z$, and x, $\frac{1}{2}-y$, z. The interpretation of these results gave for its free base (des-(oxymethylene)-lycoctonine) the structure represented by the schematic drawing and by the photograph of the molecular model.



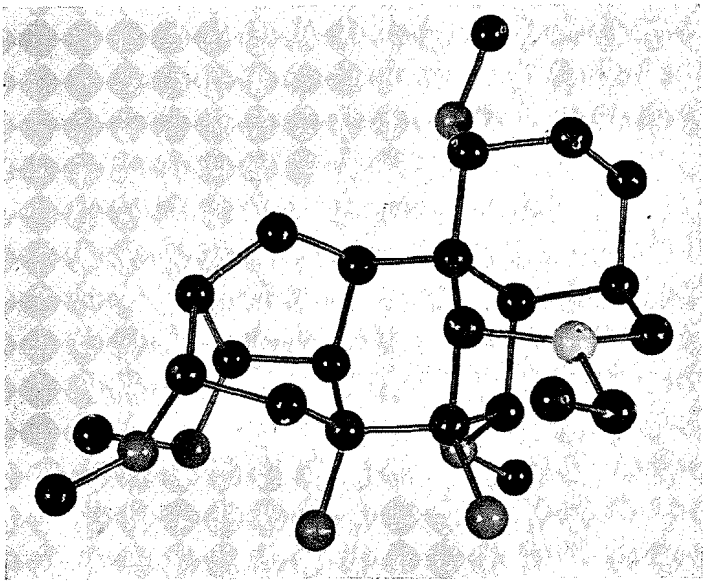


FIG. 1. The stereochemical configuration of des-(oxymethylene)-lycoctonine.

A $h0l$ difference synthesis using (F_0-F_c) as coefficients was then computed, the structure-factor calculations having been based on f values for carbon and iodine only. The pattern obtained indicated clearly all six oxygen atoms of the molecule and the oxygen atom of water of crystallization. Thus the ethyl group was identified and since it has been chemically proved to be attached to the nitrogen atom (2), the latter was indirectly located. No other chemical assumptions were made in this investigation.

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The atomic parameters were subsequently refined by Fourier and $(F_0 - F_c)$ projections along the three axes of the unit cell and the reliability index, defined as $R = \Sigma||F_0| - |F_c|| \div \Sigma|F_0|$, is now about 0.20 for each of these zones.

This work will be published in fuller detail at a later date in a different journal.

Grateful acknowledgment is made to Dr. W. H. Barnes for the use of the equipment in his laboratory and to Dr. O. E. Edwards for his interest and for the pure, chemically analyzed sample of the salt. Thanks are also due to Miss I. Ourom for her part in carrying out the computations.

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Symposium on Nuclear Chemistry and Radiochemistry

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On behalf of the conveners of the symposium I should like to acknowledge the generous co-operation of McGill University, of the National Research Council, and of the Editor-in-Chief of the Canadian Journal of Chemistry.

L. YAFFE,
CHEMISTRY DEPARTMENT,
MCGILL UNIVERSITY.

CHEMICAL EFFECTS OF THE $C^{12}(\gamma,n)C^{11}$ REACTION IN CARBONATES[1]

BY W. J. EDWARDS[2] AND K. J. MCCALLUM

ABSTRACT

The chemical effects following the carbon photoneutron reaction in calcium carbonate and sodium bicarbonate have been studied. After solution of the irradiated crystals, C^{11} was found to be present in the forms of carbonate, carbon monoxide, formic acid, oxalic acid, glyoxylic acid, and glycollic acid. The relative amounts of C^{11} appearing in each form agreed closely with those found previously for irradiations of solid sodium carbonate.

The chemical effects following the photoneutron reaction in the carbon isotope of mass 12 have been previously investigated for a few substances (1, 2). In this process, high-energy gamma rays eject a neutron from the nucleus of a carbon atom contained in a compound. The radioactive C^{11} nucleus which results possesses a high kinetic energy arising from both the momentum of the gamma ray photon and the recoil due to the emitted neutron. The C^{11} nucleus will be ejected from its parent molecule, and after being slowed down by collisions with neighboring particles, may undergo a

[1]*Manuscript received November 14, 1955.*
Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask. This work was supported by a grant from the National Research Council of Canada. This paper was presented at the Symposium on Nuclear Chemistry and Radiochemistry held at McGill University, Montreal, Que., September 7–9, 1955.
[2]*Holder of C.I.L. Fellowship, 1953–1954.*

reaction to produce a stable molecule or radical which could react with the solvent when the substance is subsequently put into solution. An investigation of the chemical forms in which the C^{11} appears in the solution gives some information concerning these processes.

Rowland and Libby (1) studied the relative amounts of C^{11} appearing in the form of carbon dioxide and carbon monoxide following the irradiation of solid and liquid carbon dioxide, solid sodium bicarbonate, and solutions of sodium bicarbonate and sodium carbonate. Gamma rays from a betatron operating at a peak energy of 48 Mev. were used. It was reported that the irradiation of samples in the solid state yielded about equal amounts of C^{11} activity in the form of each oxide, while for samples in the liquid state, 95–100% of the activity appeared as carbon monoxide.

Sharman and McCallum (2) determined the compounds containing C^{11} which were present in solutions formed from water and crystals of sodium carbonate which had been irradiated with gamma rays from a betatron operating at a peak energy of 23 Mev. The percentages of the total C^{11} activity appearing in carbon dioxide and carbon monoxide were 22% and 1% respectively, the remainder of the C^{11} being present as formic acid, oxalic acid, glyoxylic acid, and glycollic acid. The relative amounts of carbon dioxide and carbon monoxide did not agree with the suggestion of Rowland and Libby (1) that approximately equal amounts should be present in each oxide following the irradiation of solid samples.

This paper reports the results of a study of the chemical forms containing C^{11} following the irradiation of solid sodium bicarbonate and calcium carbonate with betatron gamma rays of 23 Mev. peak energy.

EXPERIMENTAL AND RESULTS

The sodium bicarbonate was Baker and Adamson reagent and was dried at 110°C. for at least 10 hr. before use. Two samples of calcium carbonate were used. The first was Merck reagent and the other consisted of calcite crystals obtained from Central Scientific Company.

The samples were exposed to radiation from a betatron operating at a peak energy of 23 Mev. for a period of 10 min. The intensity at the position of irradiation varied from 1000 to 2000 roentgens per minute in different experiments.

Decay measurements on the irradiated samples indicated the formation of O^{15} (half-life 2.5 min.), C^{11} (half-life 20.5 min.), and a small amount of a long lived activity. When sodium bicarbonate was irradiated, the long lived activity was due to Na^{24} (half-life 14.8 hr.). The long lived activity produced during the irradiation of calcium carbonate had a half-life of several hours, and amounted to about 2% of the total activity 40 min. after the end of the irradiation. The emitter was not identified. The total C^{11} activity produced in each irradiation was determined by counting weighed samples with a mica window end-on counter under standard geometry. Measurements were made 40 min. after the end of the irradiation to permit decay of the short lived O^{15}

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activity. Corrections were made for the small amount of long lived activity also present. An empirical calibration curve was used to correct for different weights of material counted.

The chemical procedures used to isolate the compounds containing C^{11} activity were similar to those used by Sharman and McCallum (2) in the study of sodium carbonate, since it was found that the same compounds were produced.

Two procedures were used to mix the carbon monoxide carrier gas with the radioactive carbon monoxide in the solution. The first method was that used previously (2) in which the carbon monoxide carrier was mixed with air or oxygen, and bubbled through the solution while acid was being added to liberate carbon dioxide from the sample. In the second method, used in addition to the first for sodium bicarbonate, the irradiated sample was placed in an evacuated flask, and the carbon monoxide carrier gas was admitted. Enough water was then introduced to dissolve the sample, and the solution was stirred vigorously with a magnetic stirrer for 10 min. to permit equilibrium of the carbon monoxide liberated in the solution with the carrier in the gas phase. Acid was then added dropwise to liberate carbon dioxide, while oxygen was passed through the flask to sweep the gases into the gas separation train. In this train, carbon monoxide and carbon dioxide were separated and isolated as previously described (2).

The procedures used to isolate and measure the radioactivity following formic acid, oxalic acid, glyoxylic acid, and glycollic acid carriers were also those previously used (2). In the experiments on calcium carbonate, the presence of the high concentration of calcium ions in the solution interfered with the isolation of some of these compounds. The calcium ions were removed either by passing the neutralized solutions through a Dowex 50 ion-exchange resin, or by precipitation as calcium carbonate.

The percentages of the C^{11} activity following the various carriers are shown in Table I. For comparison the results for sodium carbonate (2) are included in the table.

DISCUSSION

Table I shows that the distribution of the C^{11} between the different chemical forms is very closely the same for irradiations of sodium carbonate, sodium bicarbonate, and calcium carbonate. Apparently the nature and relative

TABLE I

PERCENTAGE DISTRIBUTION OF C^{11} ACTIVITY

Compound	Na_2CO_3 (2)	$CaCO_3$	$NaHCO_3$
Carbon dioxide	22±1	21±1	22±1
Carbon monoxide	1±1	1±1	1±1
Formic acid	3±1	2±1	4±1
Oxalic acid	39±1	36±1	40±1
Glyoxylic acid	24±1	29±1	24±1
Glycollic acid	10±2	12±3	10±1

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proportions of the radicals formed by the C^{11} in these crystalline carbonates are quite independent of the nature of the cation present and of the crystal structure.

The percentages of carbon dioxide and carbon monoxide containing C^{11} produced in the irradiation of sodium bicarbonate were 22% and 1% respectively. This does not agree with the result reported for the same compound by Rowland and Libby (1), who stated that approximately equal amounts of these two oxides were produced. In a private communication Rowland states that in their work the gases were liberated from the irradiated solid by boiling with a solution of sulphuric acid. He suggests that if the organic acids found in the work reported here were present in the solution, this treatment could have caused considerable decomposition of these acids, with the production of radioactive carbon monoxide and carbon dioxide. This, of course, could result in a change in the observed ratio of the two oxides, and might account for the disagreement.

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2. SHARMAN, L. J. and MCCALLUM, K. J. J. Am. Chem. Soc. 77: 2989. 1955.

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[1]*Manuscript received November 14, 1955.*
Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask. This work was supported by a grant from the National Research Council of Canada. This paper was presented at the Symposium on Nuclear Chemistry and Radiochemistry held at McGill University, Montreal, Que., September 7–9, 1955.
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THE RELATIVE YIELDS OF THE ISOTOPES OF XENON IN PLUTONIUM FISSION[1]

By W. H. Fleming and H. G. Thode

ABSTRACT

The relative fission yields of five isotopes of xenon in Pu^{239} fission have been determined. Fine structure, similar to that observed in U^{238} fission but smaller, occurs in plutonium fission in the xenon mass range. The yield of the 133 mass chain has been determined at xenon in order to permit the normalization of the relative xenon yields to the relative cesium yields.

INTRODUCTION

The first application of mass spectrometry to fission yield studies (14) showed that the mass yield curve for thermal neutron fission of U^{235} was not smooth. In particular, the yield of the 134 mass chain measured at Xe^{134} was found to be abnormally high compared to adjacent masses. More recent studies (5, 8, 11, 12, 18) employing both mass spectrometry and improved radiochemical methods have provided accurate fission yield data for the whole mass yield curve in U^{235} fission. Large deviations from a smooth curve (fine structure) are observed only in the neighborhood of the 82 neutron shell and in the region of the complementary fragments to 82 neutron shell fission products. Much smaller fine structure has been observed in the vicinity of the 50 neutron shell (15). Fine structure has also been observed in the spontaneous fission of U^{238} (2, 9, 16) and in the neutron fission of U^{233} (3, 13) and U^{238} (15).

The occurrence of fission yields differing widely from a smooth curve may be the result of a preference for a particular mass chain in the original fission process or may result from chain branching which occurs after the actual fission act. Chain branching after fission occurs by delayed neutron emission and by neutron capture processes. Corrections can be made for neutron capture processes, but, since most of the delayed neutron emitters have not been identified, correction for delayed neutron emission is difficult. It has also been suggested that additional chain branching may occur by the emission of an extra prompt neutron by fission fragments having 1, 3, 5, or 7 neutrons in excess of a closed shell after normal prompt neutron emission (4, 10).

Isotopes of xenon are the stable end products of many of the decay chains having 82 neutron members. The relative fission yields of the xenon isotopes can therefore provide considerable information about the fine structure in the mass yield curve. In addition to the stable isotopes of xenon occurring in fission, Xe^{133} and Xe^{133m} have sufficiently long half-lives to be suitable for mass spectrometric yield studies. The determination of the relative yield of the 133 mass chain at xenon makes possible the normalization of the relative yields of the isotopes of xenon to those for the cesium isotopes since Xe^{133} and Xe^{133m} subsequently decay to Cs^{133}.

[1]*Manuscript received November 16, 1955.*
Contribution from the Departments of Physics and Chemistry, Hamilton College, McMaster University, Hamilton, Ontario.

Several mechanisms have been suggested to explain the fine structure observed in the thermal neutron fission of U^{235} (4, 10, 18). The present investigation of the relative yields of xenon isotopes in Pu^{239} fission was undertaken to provide data required for the elaboration and testing of these mechanisms. In addition it was felt that a reinvestigation of the mass yield curve for Pu^{239} fission would be profitable at this time because the only available data is that obtained during the early work in the American Atomic Energy Project (1) and experimental techniques have since been greatly improved.

EXPERIMENTAL

Samples of plutonium in the form of plutonium–aluminum alloy containing approximately 10% plutonium were supplied by O. J. C. Runnalls of Atomic Energy of Canada Limited. Plutonium isotope abundance ratios for a sample of this alloy are given in Table I. Four samples containing 10 to 20 mgm. of

TABLE I

PLUTONIUM ISOTOPE ABUNDANCE SAMPLE 2 (AFTER IRRADIATION)

Isotope	Atom %
Pu^{239}	96.1
Pu^{240}	3.72
Pu^{241}	0.18

plutonium were irradiated in the N.R.X. reactor at Chalk River for a time sufficient to produce approximately 5×10^{16} fissions. Two of the samples were allowed to cool for a time sufficient for all the precursors of xenon to decay. These samples were used for the determination of the relative yields of Xe^{131}, Xe^{132}, Xe^{134}, and Xe^{136}. The remaining two samples were allowed to cool for four to five days following irradiation after which the rare gas fission products were extracted and the mass spectrometer analyses carried out. In these samples approximately one-half of the yield of the 133 mass chain was present as Xe^{133m} and Xe^{133} at the time of analysis.

The ratio of Xe^{133m} and Xe^{133} to any of the stable xenon isotopes occurring in fission can, of course, be determined mass spectrometrically. However, the presence of iodine and tellurium precursors with moderate half-lives in the 131 and 132 mass chains introduces unnecessary complications and possible errors due to uncertainty of decay schemes. While Xe^{136} has only short-lived precursors the observed yield of this isotope is strongly dependent on irradiation conditions because of the large (2.7×10^6 barns) (7) neutron capture cross section of Xe^{135}. For these reasons the yield of Xe^{133m} and Xe^{133} was only determined relative to Xe^{134} which has no long-lived precursors or other complicating factors.

Since the activity of the irradiated samples used for the determination of the relative yield of the 133 mass chain was expected to be in the neighborhood of one curie at the time of extraction it was essential that a procedure be adopted which required a minimum of handling. The extraction of the rare gas fission products was carried out by melting the irradiated Pu–Al alloy in a

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vacuum furnace. The samples could be removed from their shipping containers, opened, and the Pu–Al alloy transferred to the furnace in approximately one minute. The entire operation was carried out in a fume hood shielded with 4 in. of lead. The gases released from the melted alloy were condensed into a sample tube containing charcoal cooled to liquid air temperature and transferred to another vacuum line for purification in a calcium furnace prior to mass spectrometer analysis. The radiation from the rare gas samples themselves amounted to about 15 mr./hr. at 1 meter. Since the purification and mass spectrometer analysis involved handling the samples only for brief periods no shielding was used at this stage.

The samples were analyzed on a 180° direction focusing mass spectrometer. Magnetic scanning was employed. The ion currents were amplified by a vibrating reed electrometer and recorded on a strip chart recorder. At least 10 double scan mass spectrograms were recorded for each sample.

RESULTS

The irradiation data for the four samples used in this work and the cooling times involved are summarized in Table II. The longest lived precursor in the mass chains studied is eight day I^{131}. It is obvious that, for samples 1 and 2,

TABLE II

IRRADIATION DATA AND COOLING TIMES

Sample No.	Irradiation time (hr.)	Cooling time before extraction	Time between extraction and analysis	Approx. neutron flux, n./cm.^{2}/sec.
1	308.2	120 days	1 day	2.6×10^{12}
2	67.4	81 days	7 days	6.8×10^{12}
3	59.0	124.0 hr.	4.95 hr.	1.2×10^{13}
4	60.0	147.8 hr.	3.42 hr.	1.2×10^{13}

the observed yields need no correction for holdup along the decay chains. The relative yields of the stable xenon isotopes are given in Table III for samples 1 and 2. The Xe^{136} yields in column 6 have been corrected for neutron capture in Xe^{135} using the estimated neutron flux from Table II. In making this correction the assumption was made that the yields of the 135 and 136 mass chains in Pu^{239} fission are identical. The value of the capture cross section of Xe^{135} used in the calculations was 3.47×10^6 barns determined by comparison to the $B^{10}(n, \alpha)$ cross section (11) for an irradiation position intermediate between those in which samples 1 and 2 were irradiated. This value should be more appropriate than the monoenergetic 2200 m./sec. value of 2.7×10^6 barns (7). Because the neutron fluxes for the plutonium samples are only estimated values based on irradiation position and pile power, considerable error may be introduced into the corrected Xe^{136} yields. Additional error may arise from the assumption that the yields of the 135 and 136 mass chains are equal in plutonium fission. The deviations quoted in column 6, Table III, have been arbitrarily set at $\pm 25\%$ of the correction applied.

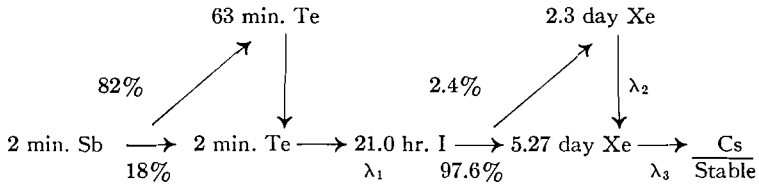
TABLE III

RELATIVE XENON YIELDS IN PLUTONIUM FISSION

Sample	Relative fission yield				
	Xe^{131}	Xe^{132}	Xe^{134}	Xe^{136}	Xe^{136} corrected
1	1.000	1.394±.002	1.978±.003	2.336±.005	1.83±.13
2	1.000	1.396±.004	1.984±.004	2.381±.003	1.70±.17

In order to calculate the relative yields of the 133 and 134 mass chains from the observed ratio of the xenon isotopes at these masses in samples 3 and 4, it is necessary that the disintegration constants of the 133 mass chain be known. A recent compilation (6) gives the following data for the 133 mass chain.

[1]



Two values are given for the half-life of I^{133} (20.5 hr., 22.4 hr.). The value 21.0 hr. has been arbitrarily chosen for use in this work. The actual value of the iodine half-life is not critical since, for the conditions of this experiment, a 10% uncertainty in this value introduces only 1% error in the final results. The times involved in the present work are such that negligible error will be introduced if the entire 133 mass chain is assumed to start at I^{133}.

Under these conditions it can readily be shown that the number of atoms of Xe^{133m} present at the time of extraction is given by

$$[2] \qquad N_2^* = 0.024R\left[\frac{(1-e^{-\lambda_1 T})e^{-\lambda_1 t_1}}{\lambda_2-\lambda_1} - \frac{\lambda_1(1-e^{-\lambda_2 T})e^{-\lambda_2 t_1}}{\lambda_2(\lambda_2-\lambda_1)}\right]$$

and the number of atoms of Xe^{133} by

$$N_3^* = 0.976R\left[\frac{(1-e^{-\lambda_1 T})e^{-\lambda_1 t_1}}{\lambda_3-\lambda_1} - \frac{\lambda_1(1-e^{-\lambda_3 T})e^{-\lambda_3 t_1}}{\lambda_3(\lambda_3-\lambda_1)}\right]$$

$$[3] \qquad + 0.024R\lambda_2\left[\frac{(1-e^{-\lambda_1 T})e^{-\lambda_1 t_1}}{(\lambda_2-\lambda_1)(\lambda_3-\lambda_1)} - \frac{\lambda_1(1-e^{-\lambda_2 T})e^{-\lambda_2 t_1}}{\lambda_2(\lambda_2-\lambda_1)(\lambda_3-\lambda_2)}\right.$$

$$\left. + \left\{\frac{1}{\lambda_2\lambda_3} + \frac{\lambda_1}{\lambda_2(\lambda_2-\lambda_1)(\lambda_3-\lambda_2)} - \frac{1}{(\lambda_2-\lambda_1)(\lambda_3-\lambda_1)}\right\}(1-e^{-\lambda_3 T})e^{-\lambda_3 t_1}\right]$$

where R is the fission rate multiplied by the fractional yield of 133 mass chain, Y^{133},

T is the irradiation time,

t_1 is the cooling time,

λ_1, λ_2, and λ_3 are as indicated in [1] above.

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From the time of extraction to analysis there is no production of Xe^{133} or Xe^{133m} from I^{133}. Therefore at the time of analysis the number of atoms of xenon of mass 133 is

$$[4] \qquad N_2 + N_3 = N_2^*\left[e^{-\lambda_2 t_2} + \frac{\lambda_2}{\lambda_3 - \lambda_2}(e^{-\lambda_2 t_2} - e^{-\lambda_3 t_2})\right] + N_3 e^{-\lambda_3 t_2}$$

where t_2 is the time between extraction and analysis.

Since the holdup in the 134 mass chain is negligible, the number of atoms of Xe^{134} at the time of analysis is R^1T where R^1 is the fission rate multiplied by the fractional yield of the 134 mass chain, Y^{134}. The relative yields of the 133 and 134 mass chains can therefore be calculated from the observed ratio

$$[5] \qquad 133/134 = (N_2 + N_3)/R^1T.$$

In practice, of course, the fission rate is not constant but varies because of pile shutdowns and variations in pile power. The effect of these variations on the final result will be small since the production rates of the 133 and 134 mass chains both vary with neutron flux in an identical manner. To provide an indication of the magnitude of this effect the calculations for sample 4 were carried through assuming a 50% decrease in flux during the last third of the irradiation time. The final result obtained differed from the value obtained assuming constant flux by only 2%.

The measured 133/134 ratios for samples 3 and 4 and the calculated yield ratios for the 133 and 134 mass chains are given in Table IV. The deviations quoted are the precision of the mass spectrometer measurements only and do

TABLE IV

RELATIVE YIELDS OF 133 AND 134 MASS CHAINS

Sample	Measured ratio $\frac{Xe^{133}+Xe^{133m}}{Xe^{134}}$	Calculated ratio Y^{133}/Y^{134}
3	0.4663±.0009	0.927±.002
4	0.4131±.0005	0.924±.001

not include possible errors arising from uncertainties in the half-lives involved in the calculations. Allowance has been made in the calculations for variation in neutron flux during the irradiations although, as stated above, the effect of such variations is small. Making allowance for possible systematic errors due to uncertainties in the decay schemes involved, it would appear reasonable to set the yield ratio of the 133 and 134 mass chains, Y^{133}/Y^{134}, equal to 0.925± .01.

DISCUSSION

Wiles *et al.* (17) have determined absolute fission yields for the heavy mass hump in Pu^{239} fission. Their value for the 133 mass chain determined at Cs^{133} is 4.97%. The xenon fission yields calculated using this value and the relative

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yield data given above are listed in Table V. The deviation shown for mass 136 arises from the uncertainty in the correction for neutron capture. The deviations at masses other than 136 arise mainly from the 133/134 yield ratio determination.

TABLE V

XENON FISSION YIELDS Pu^{239} FISSION

	Fission yield (%)	
Mass	Sample 1	Sample 2
131	2.71±.03	2.71±.03
132	3.78±.04	3.78±.04
133	4.97±.05	4.97±.05
134	5.37±.05	5.37±.05
136	5.0 ±.4	4.6 ±.5
Average value mass 136 = 4.8±.5		

Previous radiochemical yield studies (1) have given considerably higher yields for masses 131 and 132 in Pu^{239} fission (3.6% and 4.9% respectively). The possible sources of error in the present absolute value of the Cs^{133} yield are discussed by Wiles *et al.* (17). The conclusions drawn in the following discussion depend only on the relative yields of the xenon and cesium isotopes and are independent of the absolute fission yield values used. The absolute values are given only to convey some idea of the comparison between the fission yields for Pu^{239} fission and those observed with other fissioning nuclei.

Glendenin (4) suggested that the fine structure observed in the xenon mass range in U^{235} fission might be the result of chain branching due to the emission of the loosely bound 83rd neutron by the highly excited primary fission fragments having that configuration. This explanation was only in qualitative agreement with the observed yields. Pappas (10) later developed a quantitative explanation of the observed yields in U^{235} fission by combining the postulated primary fission preference for 82 neutron nuclei first suggested by Wiles (18) with a Glendenin type neutron boil-off mechanism extended to 85, 87, and 89 neutron species. In order to calculate the fission yield pattern expected on the basis of the Pappas treatment it is necessary to know the unperturbed smooth mass yield curve, the distribution of primary yields along each mass chain, and the extent of the various delayed neutron activities. There is, of course, considerable uncertainty in each of the above factors and hence the final calculated yields have a relatively large uncertainty. A comparison between the calculated and experimental xenon yields in Pu^{239} fission is shown in Fig. 1. It can be seen that the agreement is very good. Good agreement between the calculated and experimental yields has also been observed for U^{238} fission (15). However, in the case of $U^{233} + n$ fission (3) there is considerable discrepancy. Therefore it would appear that while the mechanism suggested by Pappas has considerable merit further modification is required before all experimental results can be explained.

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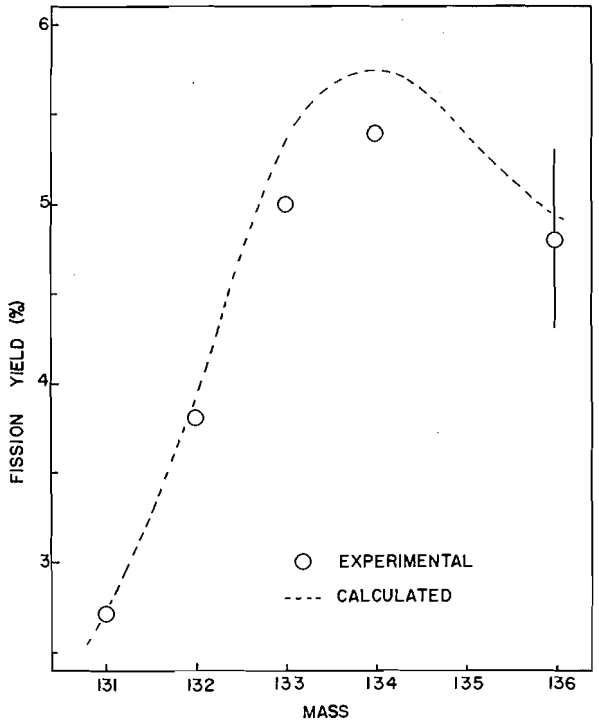

FIG. 1. Comparisons between observed plutonium fission yields and the values calculated after Pappas (10).

Further samples of Pu^{239} are now being irradiated under conditions in which neutron capture by Xe^{135} will be negligible in order to obtain a more accurate value for the yield of Xe^{136}. Possible variation of the xenon fission yields with neutron energy is also being studied.

ACKNOWLEDGMENTS

The authors are indebted to the National Research Council of Canada and to Atomic Energy of Canada Limited for financial assistance. This work would not have been possible without the wholehearted co-operation of the members of the staff of Atomic Energy of Canada Limited who supplied the samples and arranged for their irradiation.

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THE YIELD OF Cs^{138} IN THERMAL NEUTRON FISSION OF U^{235} [1]

By Rosalie M. Bartholomew and A. P. Baerg

ABSTRACT

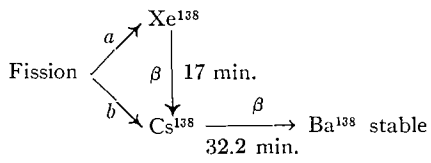
The yield of Cs^{138} in thermal neutron fission of U^{235} has been investigated using the 4π counting technique. The value obtained for the fission yield is $(7.22 \pm 0.29)\%$ based on a value of 6.32% for the fission yield of Ba^{140}. The half-life of Cs^{138} was determined and found to be 32.2 ± 0.1 min.

INTRODUCTION

Early radiochemical investigations of slow-neutron fission indicated that the familiar double-humped yield–mass curve was essentially smooth. Marked deviations from a smooth curve were definitely established, however, by Thode and co-workers (6, 11) in mass spectrometric determinations of fission product rare gases. Plausible interpretations of this fine structure have been evolved in terms of various closed shell effects on the fission process and also on the post-fission processes.

Pappas (7) has made quantitative estimates of the U^{235} fission yields in the heavy mass wing, based on the concept of primary prompt neutron emission from each fission fragment followed by additional prompt neutron emission from those fragments with 1, 3, 5, or 7 neutrons outside the closed 82 neutron shell. The estimates include, in addition, effects due to delayed neutron emission. Although only a few delayed neutron emitters have been identified, it is expected that all of them belong to a group of nuclides which have 2, 4, or 6 neutrons in excess of closed shells. The mass 138 chain is of particular interest in this connection because it may be expected to exhibit an enhanced fission yield due to delayed neutron emission from I^{139}. Pappas (7) has estimated this effect at about 5.5% of the yield estimate based on primary and secondary prompt neutron emission alone. In spite of this interesting possibility it is only very recently that measurements have been made on the yield of the mass 138 chain. We have made radiochemical measurements of the yield of 32 min. Cs^{138}, relative to that of 12.8 day Ba^{140}, in the thermal neutron fission of U^{235}, using 4π counting techniques.

The formation of Cs^{138} in fission may be represented as follows:



where the fraction of the 138 mass fragments leading to Xe^{138} is denoted by a and that leading directly to Cs^{138} by b.

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If a uranium sample is irradiated for a time, t_1, and then allowed to decay for a time, t_2, the number of Cs^{138} atoms present at time t_2 is given by:

$$[1] \quad \text{atoms } Cs^{138} = Y_{138}N\left[\frac{1-b}{\lambda_2-\lambda_1}\{e^{-\lambda_1 t_2}(1-e^{-\lambda_1 t_1}) - e^{-\lambda_2 t_2}(1-e^{-\lambda_2 t_1})\} + \frac{1}{\lambda_2}e^{-\lambda_2 t_2}(1-e^{-\lambda_2 t_1})\right]$$

where Y_{138} is the cumulative fission yield of Cs^{138}, N is the fission rate, λ_1 and λ_2 are the decay constants of Xe^{138}(17 min.) and Cs^{138}(32.2 min.) respectively. This equation may be more simply written in the form of equation [2] where k_1 and k_2 may be calculated from the experimental conditions and the known decay constants involved.

$$[2] \quad \text{atoms } Cs^{138} = Y_{138}N(k_1 b + k_2)$$

EXPERIMENTAL

Samples of uranium oxide (50–150 mgm. UO_2) were sealed in small quartz capsules and irradiated in a high flux position (about 5×10^{13} neutrons/cm.^{2}/sec.) in the Chalk River N.R.X. reactor for a few minutes and returned immediately to the laboratory by pneumatic conveyor. The capsule was crushed in 5 ml. hot 4 *N* HNO_3 solution containing about 50 mgm. Ba $(NO_3)_2$ and about 20 mgm. $CsNO_3$ carriers. The UO_2 was quickly dissolved upon the addition of HCl gas. The time of complete solution was noted as that at which the remaining Xe^{138} was removed (t_2 in equation [1]). The solution was then cooled in ice and $BaCl_2$ precipitated by saturating the solution with HCl gas. The barium was later further purified (2) for activity measurements.

The supernatant solution from the $BaCl_2$ precipitation was then diluted to 6 *N* HCl, cooled in ice, and the cesium precipitated by addition of 1 ml. of 0.125 *M* silicotungstic acid. This precipitate was washed twice with cold 6 *N* HCl and then dissolved in 2 ml. of 2 *M* LiOH and the cesium adsorbed on a Dowex-50 cation resin column (0.5 × 3 cm.) in the Li form. The column was washed with a few milliliters of water followed by 15 ml. of 1 *N* HCl. The cesium was finally removed with 5 ml. of concentrated HCl, made up to constant volume, and from this small aliquots were taken for counting.

The chemical yield of barium was determined gravimetrically by precipitation of barium sulphate. The chemical yield of cesium was determined by weighing as cesium chloroplatinate (9).

The disintegration rate of Ba^{140} and that of Cs^{138} was determined using the 4π counting technique. Counting samples were prepared by evaporation of known aliquots of the solution on thin films (5 μgm./cm.^{2}) of zapon which had a conducting film of gold (5 μgm./cm.^{2}) on each side. Self-absorption in the barium was essentially eliminated by the technique of successive dilution and by spreading the material as uniformly as possible, using insulin treated films (1).

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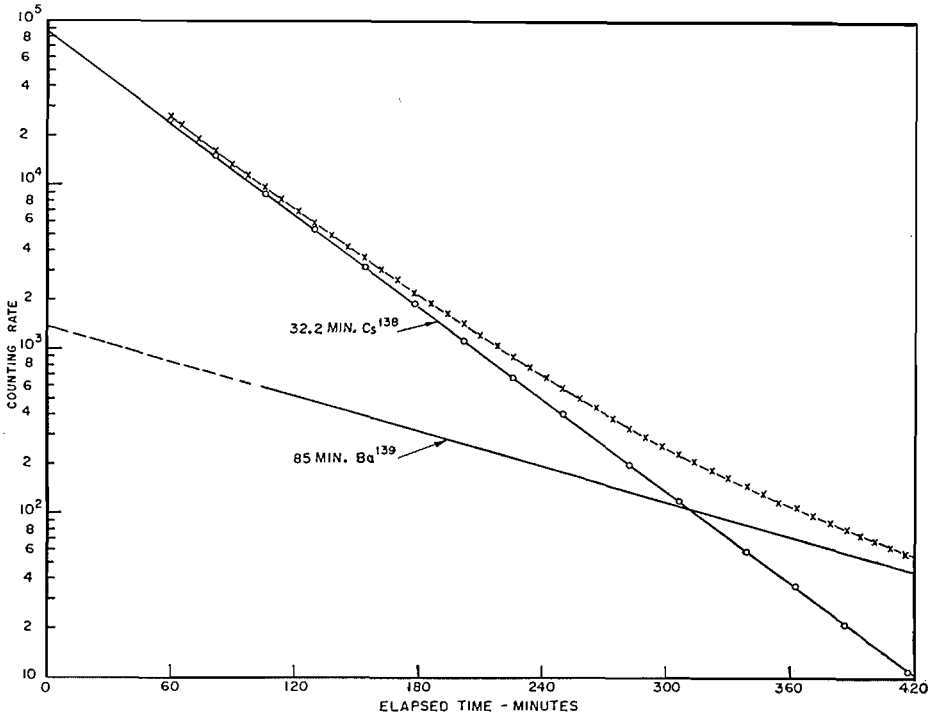

FIG. 1. Representative decay curve of a cesium source.

In Fig. 1 is shown a typical cesium source decay curve. The decay was followed for about 12 hr. to check on the purity of the Cs^{138} and to permit analysis of the curve for 85 min. Ba^{139} present in the sources as the product of the decay of some 9.7 min. Cs^{139}. The latter appears as a slightly greater counting rate at the start of the observed decay.

The disintegration rate of the Cs^{138} was calculated back to the time, t_2, at which the Xe^{138} was removed from the sample. The half-life of Cs^{138} was determined in a separate experiment in which the Cs^{139} had essentially all decayed before purification of Cs was started. The half-life found was 32.2 ± 0.1 min. over about 14 half-lives.

RESULTS AND DISCUSSION

The results of seven experiments are summarized in Table I. The value obtained for the fission yield of Cs^{138} is 7.22% with a standard deviation of 0.29%. In the yield calculations it was assumed that the fractional independent yield, b, for Cs is zero. Experimental conditions were varied so as to obtain a range of the ratio k_1/k_2. It is felt that this ratio varied sufficiently that an independent yield of Cs^{138} greater than 5% of the chain yield would have been detected. The independent yield of Cs^{138} may, however, be estimated to be about 20% of the chain yield before secondary prompt neutron emission, assuming the most probable charge, Zp, for the 138 mass chain to be 53.9.

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TABLE I

EXPERIMENTAL RESULTS

atoms $Cs^{138} = Y_{138}N(k_1b + k_2)$

Expt. No.	Irradiation time, t_1 (sec.)	Decay time, t_2 (sec.)	k_1	k_2	k_1/k_2	Fission yield (%) (relative to Ba^{140} = 6.32%)
1	180	632	79.61	59.34	1.34	6.65
2	180	1170	33.95	80.61	0.43	6.97
3	300	1260	41.76	139.22	0.30	7.58
4	300	1275	40.42	139.60	0.29	7.25
5	300	1730	6.42	146.48	0.044	7.34
6	180	726	68.85	65.46	1.07	7.39
7	300	2250	−17.27	144.14	−0.12	7.36

Average = 7.22±0.29%

Pappas (7) has postulated that those nuclides with 83, 85, 87, and 89 neutrons which are formed independently in fission are removed from their mass chains by additional prompt neutron emission. Since the Cs^{138} nucleus contains 83 neutrons no observable independent yield would be expected. Our results are consistent with these ideas.

The value of 7.22% for the yield of Cs^{138} is considerably greater than that of 6.8% for the chain predicted by Pappas and it deviates markedly from the unpublished mass spectrometer value of 5.74% quoted by Steinberg and Glendenin (10) in their paper to the Geneva conference. Unless the accepted decay scheme (3) for Cs^{138} is incorrect it is difficult to account for this discrepancy at the present time. On the other hand a reasonable interpretation for the 7.22% value can be made in terms of delayed neutron emission in I^{139}.

If the 2.6 sec. I^{139} is not a delayed neutron emitter the predicted yield of the mass 138 chain would be about 6.44%, not significantly different from the yield of about 6.3% predicted from the smooth mass–yield curve. The estimated independent yield of I^{139} is 1.36% in fission assuming that the most probable mass 139 charge, Zp, is 54.3. Pappas has estimated that about 25% of the β-emission in I^{139} leads to neutron emission in the excited Xe^{139} daughter. This brings the estimated yield for mass 138 up to 6.8%. The neutron emission probability for I^{139} would have to be about 56% to bring the mass 138 yield to 7.22%. The yield of the mass 139 chain should then also be correspondingly lower—about 5.6%. Earlier radiochemical measurements on Ba^{139} indicated values of 5.9 and 6.1% (see Ref. 7). Reed and Turkevich (8) have found a value of 6.4% while Pappas (7) has measured the yield as 5.79%.

It seems significant that a recent analysis, at Los Alamos and Brookhaven, of the gross decay curve for delayed neutrons in U^{235} fission indicates a 2.11 sec. period with over 40% abundance (5). The total yield of delayed neutrons in U^{235} fission is about 0.755% of all neutrons (4). If this 2.11 sec. delayed neutron period, with its 40% abundance, is ascribed to I^{139}, the total yield of the mass 138 chain becomes 7.21%.

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RECENT DEVELOPMENTS IN LOW BACKGROUND GEIGER–MÜLLER COUNTERS[1]

By W. E. Grummitt,[2] R. M. Brown,[3] A. J. Cruikshank,[3] and I. L. Fowler[2]

ABSTRACT

G–M counting assemblies have been constructed which give dependable low background operation in routine use. Possible construction materials have been examined in detail for radioactive content in an effort to achieve minimum inherent activity in the assembly. The cosmic ray component of the normal background has been eliminated by an anticoincidence arrangement. Increased reliability of the system is obtained through (*a*) use of a multiple anode anticoincidence counter in place of a bundle of tubes, (*b*) use of an electronic quench on both sample and shielding counters, and (*c*) operation of the assembly as flow counters in tandem. In the best arrangement to date a copper counter with a polystyrene seal gives a background of 0.9 counts per minute.

INTRODUCTION

There has been considerable information published during the last few years by workers using 1 to 10 liter gas filled counters to measure very low C^{14} and tritium activities (1, 4, 7). The present paper considers the design of a low background assembly suitable for use with a conventional end-window beta or 60 cc. tritium counter.

The data at present available indicate that three components contribute to the background in a counter: cosmic radiation, γ disintegrations in the shield and surrounding material, and α, β, and γ activities in the counter materials. The cosmic contribution can be eliminated electronically by rejecting pulses which occur coincidently with those in surrounding counters. Because of the present low efficiency of γ counting, this method cannot be used to eliminate the second component of the background and it is therefore necessary to shield against γ radiation. The third component must be controlled by careful selection of construction materials.

Very little information is available regarding radioactive impurities in metals and common insulating materials. Anderson, Arnold, and Libby (1) give some qualitative data for iron, steel, and brass, while Bearden (2) and more recently Fergusson (4) have measured the α counting rate of some metal surfaces. It is desirable to investigate such materials in some detail in order to be able to construct an assembly having minimum inherent radioactivity.

COUNTER MATERIALS

Two methods of examining materials are of value, direct counting of a sample of large area and chemical concentration of the radioactive contami-

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[2]*Atomic Energy of Canada Limited, Chalk River, Ontario.*
[3]*Defence Research Chemical Laboratories, Ottawa, Canada.*

nant. In the first instance the activity of the sample is compared with a known uncontaminated control. In the second, the sample is dissolved in acid and scavenging agents such as ferric hydroxide – barium carbonate precipitated by the addition of a suitable reagent. If the ferric hydroxide is counted in high geometry, the sensitivity can be increased 100-fold over direct counting. The K^{40} contribution is estimated from spectrographic analyses, although its contribution is negligible for metals. The β activity of plastics is readily measured by destructive distillation of the material in a covered nickel crucible and counting the ash.

Results obtained for a wide variety of materials are presented in Table I. Copper is superior to the other metals measured, probably as a result of

TABLE I

ACTIVITIES IN COUNTER MATERIALS

	Dis./min./100 gm.	β^- counts/min./100 cm.^{2}
Lead, modern	350	11
Lead, 16th century	35	1
Solder, 30/70 Fluxrite	220	7
Solder, 50/50 Wire	700	23
Aluminum 2S	160	6
Aluminum superpure	110	4
Brass rod	60	2
Brass tubing	4, 8, 16	0.1, 0.3, 0.5
Hard solder	50	1.5
Copper, OFHC tubing	1.5	0.05
Polystyrene sheet	0.7	0.02
Polythene sheet	0.8	0.025
Perspex sheet, ICI	0.4	0.01
Plexiglas sheet, Rohm and Haas, UVA	0.7	0.02
Plexiglas sheet, Rohm and Haas, Transparent	1.0	0.03
Lucite rod, Dupont	0.5	0.015
Corning 7750 sealing glass		43
Corning 7052 glass		93
Corning 7740 Pyrex glass		7
Corning 0080 Soda Lime glass		7
Silica		0.3
Steel scale		5
Mica, India Ruby (10 mgm./cm.^{2})		30

electrolytic refining. Numerous metals not included in the table, e.g. platinum, tin, cadmium, and antimony, have a rather high and variable level of activity. Values ranging between 10 and 200 c.p.m./100 cm.^{2} are observed. It is interesting to note that 16th century lead is appreciably better than 'superpure' aluminum.

There is extremely little variation in the activity remaining in the ash of various plastics. This is somewhat surprising since the ash weight varies from 1.7 mgm./100 gm. for Plexiglas UVA (ultraviolet absorbing) to 90 mgm./100 gm. for polythene. The present level for local dust is 25 dis./min./100 mgm. ash, comparable to the specific activity of Plexiglas ash.

Using a β/α ratio of 20, an average of that observed for aluminum, old lead, and local sand, it is possible to obtain a measure of the surface α activity.

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Calculated counting rates range from 3×10^{-3} c.p.m./100 cm.^{2} for oxygen-free copper to 6×10^{-4} for Perspex and Lucite. These values are a factor of 5 to 15 lower than those observed on counting "radioactively clean" materials (4, 2), and presumably represent minimal values which would be obtained for samples completely free from surface contamination.

SHIELDING MATERIALS

Numerous materials are in common use as γ ray shields and there are advantages associated with each. Radioactive impurities in lead, copper, and mercury can be estimated readily but this is more difficult with iron. In this case the shield is usually constructed and then tested for contamination by comparison with other shields. Lead is easily cast to shape and has a high density, but modern samples contain appreciable activities. The observed level of activity in old lead is presumably due to radium, while the major portion of the activity in modern lead is due to Pb^{210}. Using the ratio of activities in the two lead samples it is possible to calculate that the extent of removal of radium in the 16th century refining process was 96%, assuming that the original ores contained similar amounts of radium. Mercury is obtainable in very pure form, but requires a complex safe containing vessel and is expensive. The cost can be reduced by a factor of two to three by interposing the mercury between the counters. This may improve the background, but demands larger and somewhat more complex annular and top counters because of the increased radius.

A comparison of the backgrounds obtainable with lead and mercury is of interest. The best value achieved to date is 0.9 c.p.m. in a 30 cc. counter in a castle of 2 in. of mercury surrounded by 2 in. of modern lead. With the mercury removed this count increased to 1.8, a difference of 0.9 c.p.m. Since 16th century lead shows an improvement of 10 times over modern lead (Table I), the count inside 2 in. of 16th century lead surrounded by 2 in. of modern lead would be 1.0, an increase of only 0.1 c.p.m. over the mercury–lead combination. For a small counter such as the one used here, lead can provide a very satisfactory and economical solution.

COUNTERS

The end-window β counter shown in Fig. 1 is constructed of 0.1 in. oxygen-free copper tubing to which the copper end cap and flange are hard soldered. A polystyrene insulator which carries the tungsten or stainless steel center wire is cemented in place in the end cap with Biggs R313 or Armstrong A1 or A2 bonding agent.* There is some evidence that polystyrene is porous to hydrogen, helium, and possibly air. It has been found difficult to make counters with such insulators last for six months. Saran insulators appear to be much better. Mica is used as a window material for counters which are to be evacuated and filled, but a thin plastic such as saran film is used in flow counters which operate at atmospheric pressure. In both instances the windows are cemented in place and covered with a thin conducting film of aquadag to minimize charge effects which result in a form of instability.

*Carl H. Biggs Co., Los Angeles, California. Armstrong Products Co., Warsaw, Indiana.

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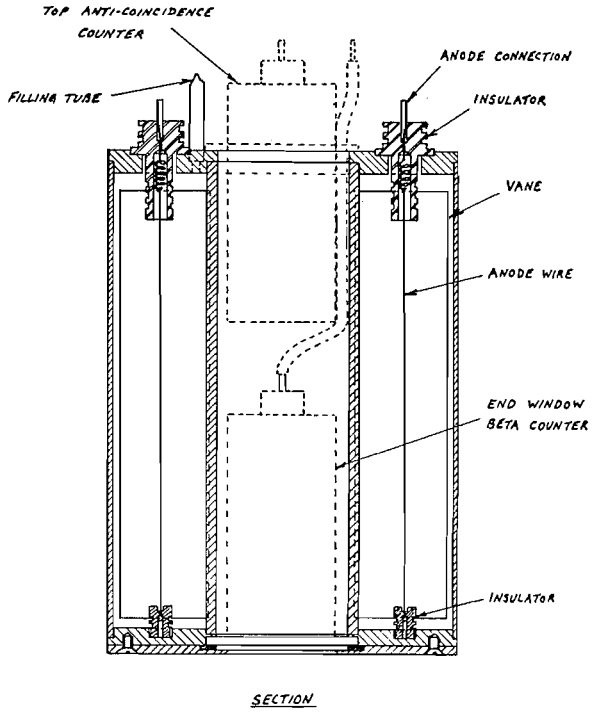

FIG. 1. Anticoincidence counter assembly.

The top anticoincidence counter is constructed in a similar manner except that the window is replaced with a copper plate. In the 60 cc. tritium internal gas counter construction is again similar but the wire is supported at both ends by having insulators in both end caps.

Initially, six separate shielding counters were used but these have been replaced with a multiple anode annular counter which has previously been described in detail (5). It is again constructed of copper with polystyrene insulators and eight wires are symmetrically disposed in a common envelope consisting of the annular volume between two concentric cylinders. As suggested by Raeth (6), shielding vanes may be interposed between the wires. These improve the plateau characteristics and allow the wires to operate independently of one another. However they constitute a small amount of dead volume and interfere with flushing when the assembly is used as a flow counter. Photographs of a sectioned early model of this counter are shown in Fig. 2.

In the operation of the assembly all the shielding counters are connected together and placed in anticoincidence with the end-window β counter or the 60 cc. tritium counter.

The anticoincidence background is, of course, a function of the coincident background and as this varies directly with the efficiency of the counters for cosmic rays, the stability of the latter is of the utmost importance. Thus if the

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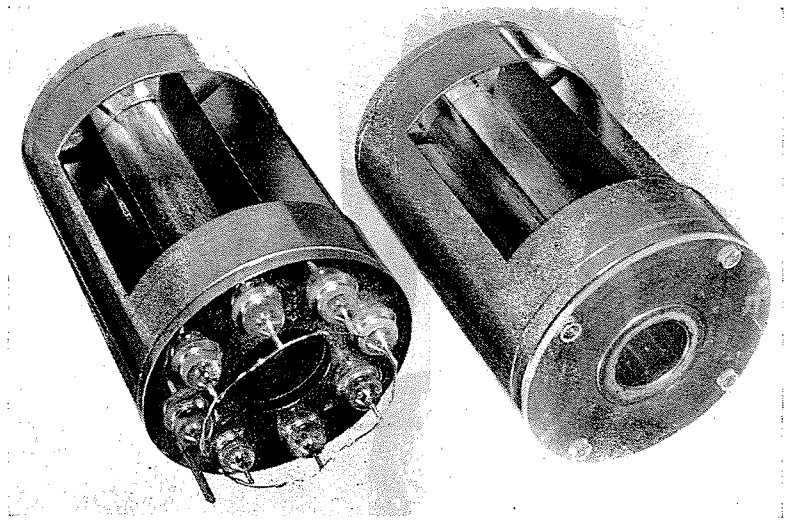

FIG. 2. Cutaway view of anticoincidence counter assembly.

anticoincidence background is equal to 1, and the coincident* equal to 10, a 1% change in the efficiency of the shielding counters will cause a 10% change in the anticoincidence background. An anticoincidence annular counter greatly increases the reliability of the system, being much more stable than six individual counters and having a relatively constant efficiency throughout its useful life. Furthermore if it fails, failure is immediately apparent. Failure of one counter from a ring of six separate counters connected together might go unnoticed for a considerable time.

COUNTER OPERATION

The use of an electronic quench unit (3) is found to be advantageous even with self-quenched G–M counters. During the discharge of such a counter, most of the positive charges are transferred from the noble gas atoms to the molecules of quench gas which dissociate on reaching the cathode thus avoiding photoemission of electrons by the cathode and subsequent secondary discharge of the counter. However, the concentration of quench gas may be insufficient to completely remove the positively charged noble gas ions, in which case a number of secondary spurious pulses may be expected. These are most likely to occur when the quench gas has been depleted by a large number of discharges, or when it is desired to introduce high pressures of some additional gas such as hydrogen. If a trace of air leaks into the counter spurious discharges may also result from oxygen negative-ion formation. Because of their lower mobility the negative ions may only reach the neighborhood of the wire after the discharge in which they were formed is complete and thus trigger a second and spurious discharge. To eliminate these spurious pulses the counter may be electronically quenched, holding the potential of the wire below threshold voltage after a discharge for a period longer than the

**The coincident background is that portion which is coincident in both counters and is removed by the anticoincidence circuit. The anticoincidence background is the portion remaining.*

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transit time of the ions involved. This time is about 200 μsec. for hydrogen in a 1 in. diameter counter. In practice dead times of the order of 1000 to 2000 μsec. are used for both counters. Since the dead time is fixed by the quench unit and is always the same, counting losses due to it may be calculated with accuracy.

Wolfgang and Libby (7) have introduced the use of ethylene as a quench gas for hydrogen, suggesting that the charge transfer action is one of chemical absorption of the negative hydrogen ions. However, the system gives satisfactory counting characteristics only at limited hydrogen pressures. The beneficial effect of applying an electronic quench to this counting system is illustrated in Fig. 3. A flat plateau has been obtained with hydrogen pressures

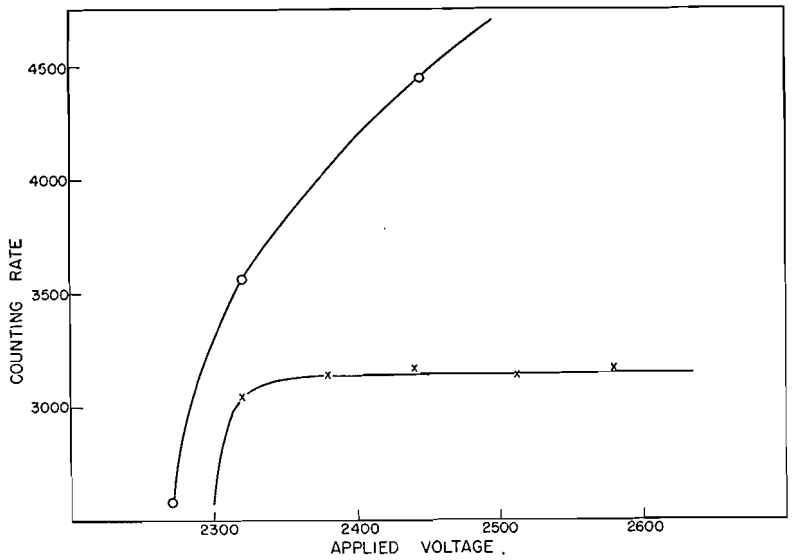

FIG. 3. Typical plateaus.
×—With external quench ○—Without external quench
Filling—6 cm. argon, 4 cm. ethylene, 40 cm. hydrogen.

up to 70 cm. Hg and there is every indication that considerably higher pressures could be used successfully with this circuit.

As the arrangement of shielding counters is unusual, a determination was made of the effectiveness of their distribution. Fig. 4 shows the effect of the vertical position of the end-window counter within the assembly as illustrated in Fig. 1. An increase in background is observed because of incomplete shielding from below (left), and because of incomplete top shielding (right) as the center counters are raised. A redesign of the annular ring which would lower its effective counting volume would thus be desirable. In a more recent model the effective volume has been lowered 0.42 in. by decreasing the thickness of the end plate and the projecting length of the bottom insulators.

One of the problems associated with the operation of G–M counters is the relatively short life expectancy* and this is accentuated in a low background

**Halogen quenched counters have very long lives but because of their somewhat lower cosmic ray efficiency and a delay phenomenon they are not suitable in anticoincidence arrangements.*

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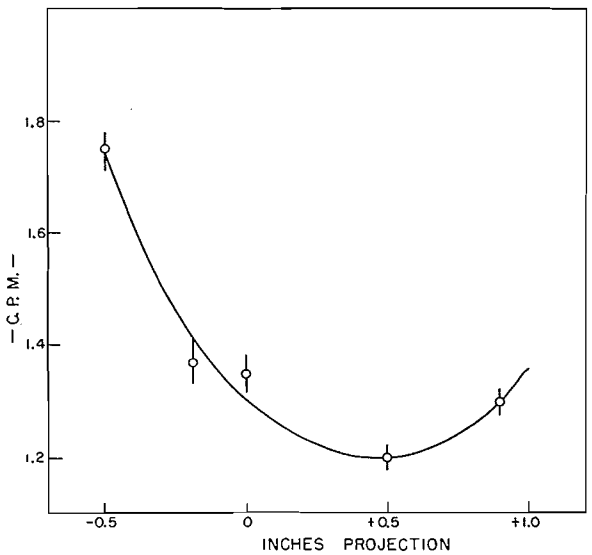

FIG. 4. Effect of the position of the center counter within the annular counter.

anticoincidence assembly because of the multiplicity of counters and limitations regarding materials. The use of the multiple anode counter substantially reduces the magnitude of this problem but a further improvement has been obtained by the operation of the whole assembly as flow counters in series using an isobutane–helium mixture. Fig. 5 shows the dependence of the G–M

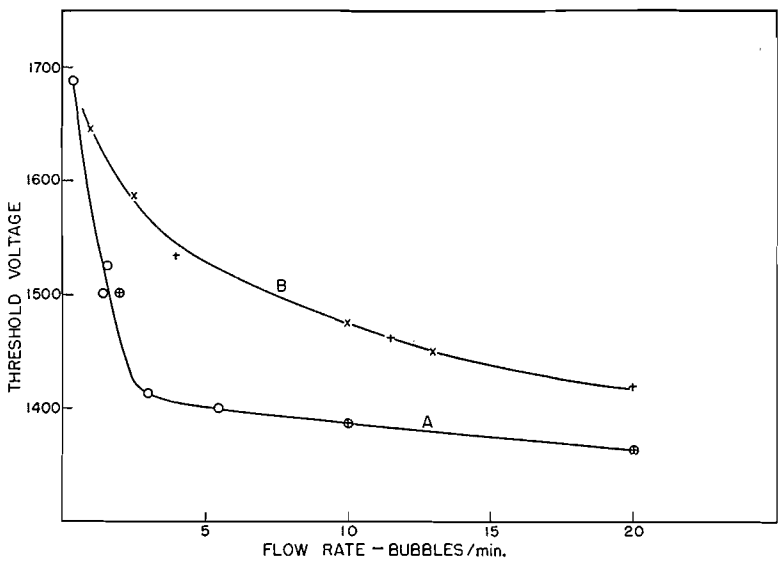

FIG. 5. Geiger threshold as a function of the rate of flow of gas through the counter.
⊕+—Increased flow ○×—Decreased flow

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threshold on the gas flow rate, the lower curve being obtained with the multiple anode counter. It is desirable, of course, to operate in a region of minimum slope and consequently rates as low as five bubbles per minute (1 cc./min.) are satisfactory. The upper curve shows the deterioration of plateau length and slope by the introduction of 1 ft. of tygon tubing (a plasticized polyvinyl copolymer). At 1 cc./min. the plateau slope is increased from 2% to 14% per 100 v. This is typical of the effect of chlorinated hydrocarbons and is presumably due to negative-ion formation.

The increased life expected from the flow system will also result in a more stable counter because of the removal of two aging phenomena: increasing spurious counts in the end-window counter and increasing threshold voltage. Furthermore, plastic film can be substituted for the mica window, removing the last major source of activity from the counter and making the background of an end-window counter comparable with that obtainable in a gas counter.

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PRODUCTION OF Be^7 IN THE ATMOSPHERE[1]

By A. J. Cruikshank,[2] G. Cowper,[3] and W. E. Grummitt[3]

ABSTRACT

The concentration of Be^7 in the atmosphere has been determined by measuring the activity associated with dust particles in ground level air. It is calculated that the observed concentration is maintained by a production rate of 2300 atoms $Be^7/cm.^2/day$ in northern latitudes.

Libby (4) in 1946 predicted the presence of radioactive nuclides in the atmosphere. C^{14} and H^3 have been widely studied and Be^7 has been reported recently in rain by Arnold and Al-Salih (1). We have investigated the Be^7 attached to dust particles in the air and calculate a production rate of 2300 atoms $cm.^{-2}$ day^{-1}. This is somewhat smaller than but compatible with Arnold's value from rain.

EXPERIMENTAL

Samples were collected over a period of 14 months at four widely separated stations north of geomagnetic latitude 55°. Air volumes of 10^7–10^8 liters were passed through efficient paper filters which removed essentially all of the mass of the dust in the atmosphere. The papers were ashed at 500°C. and inactive Be and Ce carriers were added. The mixture was fused with $NaHSO_4$, then digested with water, and treated with NH_3. The precipitate was dissolved in HCl and reprecipitated several times with NH_3 gas to remove excess $CaSO_4$ and SiO_2. A few milligrams $SbCl_3$ were added and precipitated with H_2S from slightly acid solution to remove interfering activities such as Ru and Te. A further NH_3 precipitation followed by solution in a minimum of HCl left further sulphides behind. Ce was precipitated from 3 *N* NaOH and Be was recovered by acidifying the solution and then precipitating with NH_3.

The $Ce(OH)_3$ was successively precipitated as fluoride, hydroxide, and oxalate. The oxalate was mounted, weighed, and beta counted through absorbers to estimate the Pr^{144} activity. This was used as a measure of the long lived fission products collected.

The $Be(OH)_2$ was dissolved in dilute HCl and scavenged twice with $Fe(OH)_3$ precipitated from 1.5 *N* NaOH. Be was then precipitated with NH_4OH, converted to the basic acetate by heating with acetic acid to 200°C., and then was extracted into $CHCl_3$. The $CHCl_3$ was evaporated, $Be(OH)_2$ was precipitated, ignited at 500°C., and weighed.

The 0.48 Mev. γ ray was counted in the central well of a 3 in. NaI crystal which was shielded with 2 in. Hg and 4 in. Pb. An 18 channel pulse analyzer

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[2]*Defence Research Chemical Laboratories, Ottawa, Canada.*
[3]*Atomic Energy of Canada Limited, Chalk River, Ontario.*

was used to scan the peak. Energy and efficiency calibrations were done with standardized Na^{22} and Cs^{137} sources. The Be^7 concentration at the time of collection was calculated using a 53 day half-life, γ counting efficiency of 0.50, and γ branching ratio of 0.11.

Several early samples showed Ru γ activity, but introduction of the sulphide scavenge and an extra $Fe(OH)_3$ scavenge produced pure Be activity. Three samples were put through the complete purification for a second time and showed the same specific activity. The yield of Be was usually 60–70% but in some samples containing an excessive amount (>100 mgm.) of Al much Be was lost in the acetate extraction and only 15–20% over-all yield was obtained.

In some cases where there was a considerable delay in analyzing the samples, the counting rates were low compared to the background and there is considerable statistical error.

RESULTS

The observed Be^7 and Ce^{144} concentrations in atoms per liter are given in Tables I and II. They are corrected for decay to the time of collection. The

TABLE I

ATOM CONCENTRATIONS IN THE ATMOSPHERE IN ATOMS/LITER AT THE TIME OF COLLECTION

Date	Station 1		Station 2	
	Be^7	Ce^{144}	Be^7	Ce^{144}
Nov.	0±20	7.6	60±50	1.0
Dec.	23±2.5		5.3±2.5	
Jan.	10.7±2.5	2.9	3.9±2.1	1.9
Feb.	25±4	1	14±4	
Mar.	13±2.5		12±2.5	
Apr.	27±3.7		16±3	
May	5.5±1.2		14±1.2	1.2
May	17±1.9	0.8	10±1.6	
June	10.5±2		15±1.1	7.3
June	17.7±1.7	7.8		
July	8.8±0.9	5.6	10.6±2.2	8.9
Aug.	1.0±1	1.2	2.5±1.0	1.0
Sept.	1.8±0.6	5.5	5.1±0.8	8.2
Oct.			4.7±0.5	11.5
Nov.			8.0±0.4	37.2
Dec.			7.1±0.2	40

TABLE II

ATOM CONCENTRATIONS IN THE ATMOSPHERE IN ATOMS/LITER AT THE TIME OF COLLECTION

Date	Be^7	Ce^{144}
Station 3		
27 July – 3 Aug.	1.6±0.12	10
15 Oct. – 25 Oct.	1.8±0.13	35.4
7 Jan. – 17 Jan.	2.6±0.05	34.6
Station 4		
5 Jan. – 8 Jan.	4.2±0.25	13.6

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stations are numbered from north to south. The limits of error given are the standard deviations of the counting rates, usually the principal source of error. Another source of error, the magnitude of which is difficult to estimate, is the plugging of the filter by an overload of dust or by small amounts of driven snow. Filters which were obviously snowbound were discarded. At Stations 3 and 4 about four times as much air was put through each filter as at Stations 1 and 2, and the dust loading was somewhat higher, so that less than the calculated volume may have been filtered. Hence the concentrations reported for Stations 3 and 4 may be somewhat low.

There is a considerable day-to-day variation in both Be and Ce concentrations and also a marked seasonal variation from winter to summer at Stations 1 and 2. The variation is greater at Station 1 than at Station 2 and at Station 3 there is little seasonal variation.

DISCUSSION

If the Be and Ce were produced artificially one would expect that subsequently the Be activity would decrease relative to the Ce, because of the difference in half-lives. This is not observed, so we conclude that Be^7 is produced naturally by the action of high energy cosmic rays in the atmosphere.

This being so, one would expect that the concentration would build up to an equilibrium value corresponding to the rate of production. However diffusion, gravity, electrostatic attraction, and rainfall will reduce the concentration by bringing the Be^7 to the earth's surface where it becomes fixed. Of these, rain and snow are by far the most efficient in removing dust from the air and Arnold has shown the presence of Be^7 in rain.

Day-to-day variation can probably be explained in terms of atmospheric stability as in studies of industrial air pollution. We will attempt to show that rain and snowfall can account for the seasonal variations in a satisfactory manner and thus arrive at an average value for the rate of production.

Since the yearly average Be^7 concentrations at Stations 1 and 2 are roughly equal and the total annual precipitation at 2 is three times that at 1, the total precipitation cannot be an important factor. We have introduced as the significant variable the function R, which equals the amount of rain or snow in the month previous to collection divided by the total annual rainfall. The physical basis for this is the assumption that the cleanup is proportional to the fraction of the available water which comes down as rain or snow. In cold climates with little water vapor, a small amount of rain may include nearly all the dust nuclei present, whereas in a warmer climate the same amount of rain may represent a much larger number of drops, many of which evaporate before reaching the ground, thus leaving their nuclei behind. The annual rainfall is taken as a rough measure of the absolute humidity.

The curves in Fig. 1 show the reciprocal of R, and the points are the Be^7 concentrations in atoms per liter. The points follow the curves fairly well but with an apparent time lag.

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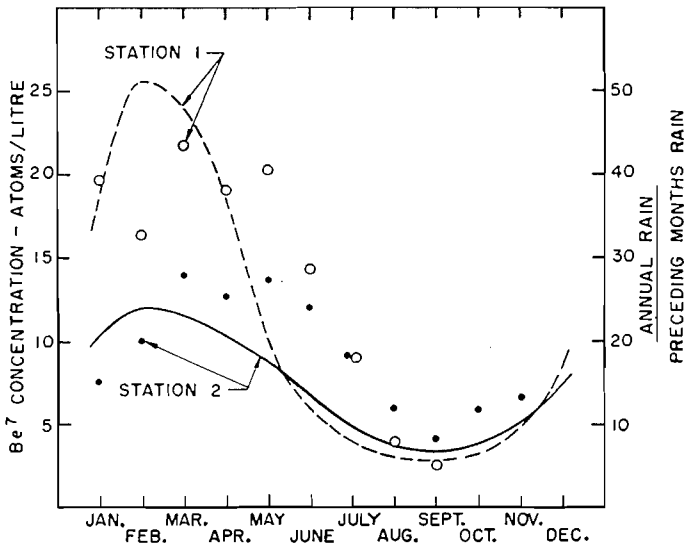

FIG. 1. Monthly variation of Be^7 concentration with rainfall. The curves indicate the fraction of the total annual precipitation which fell in the preceding month and the points indicate Be^7 concentration.

Consider the usual type of differential equation

$$dN/dt = Q - \Lambda N$$

where N = concentration of Be^7 in atoms liter^{-1}
Q = rate of formation of Be^7 in atoms liter^{-1} day^{-1}
Λ = rate of disappearance of Be^7
$\equiv \lambda + kR$
λ = disintegration constant of Be^7 in day^{-1}.

Integrated, this becomes

$$N_t = N_0 e^{-\Lambda t} + Q(1 - e^{-\Lambda t})/\Lambda$$

and at saturation

$$Q = \Lambda N$$

or

$$1/N = \lambda/Q + kR/Q.$$

At Stations 1 and 2, the winter snowfall is very low and equilibrium is approached slowly in the spring quarter with a period approximating $1/\lambda$. In the summer R is large, Λ becomes large, and equilibrium is quickly established.

Fig. 2 shows the reciprocal of the quarterly average Be^7 concentrations (slightly corrected for non-equilibrium conditions) plotted against R. The intercept gives $1/N = \lambda/Q = 0.02$ from which $Q = 0.655$ atom liter^{-1} day^{-1} and the slope gives $k/Q = 1.3$ or $k = 0.86$ day^{-1}. As the intercept is very close to zero there is some uncertainty in the value of Q.

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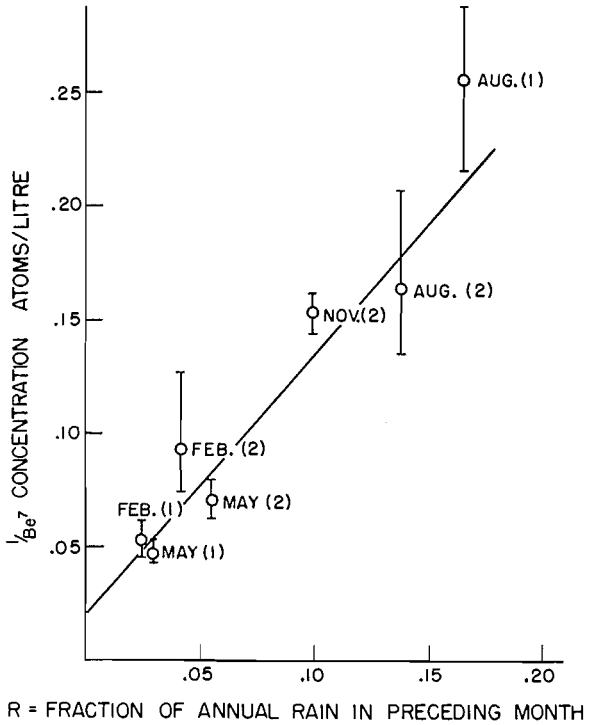

FIG. 2. Variation of Be^7 concentration with rainfall. Quarterly averages at Stations 1 and 2.

Substituting these values in the growth equation gives the Be^7 concentrations in the "N_{calc}" column of Table III. The agreement with the observed figures at Stations 1 and 2 is fairly good. At Station 3 the observed values

TABLE III

COMPARISON OF CALCULATED AND OBSERVED Be^7 CONCENTRATIONS

Month	Three month averages				Obs. values, Station 3	
	Station 1		Station 2			
	N_{calc}	N_{obs}/N_{calc}	N_{calc}	N_{obs}/N_{calc}	N_{calc}	N_{obs}/N_{calc}
Jan.	14.1	1.39	12.0	0.64	8.1	0.32
Feb.	17.1	0.95	13.5	0.74		
Mar.	18.2	1.19	13.1	1.07		
Apr.	20.4	0.93	11.9	1.17		
May	18.9	1.07	10.8	1.39		
June	16.7	0.86	9.2	1.41		
July	10.1	0.89	7.3	1.27		
Aug.	7.2	0.54	5.2	1.17	6.6	0.24
Sept.	4.4	(0.80)	4.7	0.87		
Oct.	4.7		5.4	1.09	7.5	0.24
Nov.	7.0		7.2	0.92		
Year	12.56	0.95	9.16	1.03		

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may be low because of the overestimate of the air volumes mentioned earlier. The effective Q may be lower as well, because of considerable mixing with air from the Gulf of Mexico where the cosmic ray intensity is less.

In order to calculate the total rate of production of Be^7 to the top of the atmosphere we must make some assumptions as to the structure of the atmosphere and the mode of production of Be^7. The following assumptions are qualitative and do not apply rigorously to any given case. There is uniform vertical mixing in the troposphere to 40,000 ft. (200 mb.). There is a loss close to the ground due to the settling of dust in the absence of rain. This effect is being investigated further, but aircraft flights have shown that our ground level values are one half those in the bulk of the troposphere. The volume of the troposphere is assumed to be 640 liters/cm^2. The production rate in the troposphere is thus $2 \times 640 \times 0.655 = 840$ atoms cm.$^{-2}$ day^{-1} for northern latitudes, ignoring north–south mixing.

The contribution from the stratosphere is mainly by gravitational fall from the twilight zone (200–50 mb.). Vertical diffusion is very slow as shown by the relative humidity of 2–3% compared with nearly 100% a few kilometers lower in the troposphere (2). However this low humidity implies a circulation of about six months from the equator which means that the concentration will be affected slightly by the lower cosmic ray intensity below 50° latitude. Above 50 mb., there is probably no dust and hence the fallout time is very long compared with 53 days. It has been observed that volcanic ash in the stratosphere falls at 86 meters/day and from this we estimate a half time of about 85 days for fallout of Be^7 through the 200 mb. level.

The Be^7 is presumably formed by reactions such as $N^{14}(p,2\alpha)Be^7$. There are a large number of such reactions, all roughly equal in probability at high energies. The distribution of high energy nucleons in the atmosphere is fairly well known (3) and assuming that Be^7 production is proportional to the flux, one can estimate that 20% of the total is formed below the 200 mb. level and 48% between the 200 and 50 mb. levels. Allowing for the fallout time from the stratosphere, the troposphere concentration should be $0.20 + 0.33 \times 0.48 = 0.36$ times the total. Thus the total Be^7 production to the top of the atmosphere in northern latitudes is $840/0.36 \approx 2300$ atoms cm.$^{-2}$ day^{-1}.

H. Carmichael in a private communication has used data for star production in ion chambers to estimate a production rate for Be^7 of 1.1×10^4 atoms cm.$^{-2}$ day^{-1} for northern latitudes.

This value and Arnold's value of 3000 atoms cm.$^{-2}$ day^{-1} agree fairly well with ours, considering the differing assumptions made in each calculation.

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THE DETERMINATION OF TRITIUM IN NATURAL WATERS[1]

By R. M. Brown[2] and W. E. Grummitt[3]

ABSTRACT

A study of the tritium content of rain- and sea-water samples collected during the past several years has been made. The tritium in 100–2000 gm. samples was concentrated 2000 to 20000 fold by electrolysis and the final concentrate counted as hydrogen in a Geiger counter. Good counter characteristics were obtained at hydrogen pressures up to one atmosphere by the use of an electronic quench unit of suitable deadtime in addition to the internal quench gas, ethylene. Rain and snow samples collected at Ottawa over the period 1951–1953 were found to range from 17.1 to 42.0 tritium atoms per 10^{18} hydrogen atoms, averaging 26.6. Tritium values for Ottawa rain-water for 1954 showed marked effects of the thermonuclear tests in the Pacific in the spring of that year, rising 10 to 100 fold during the test period, then gradually returning to normal, demonstrating a half time for washout of 35 days. The average tritium concentration of the year's rain is estimated to be 260×10^{-18} T/H. Surface sea-water samples collected at widely separated sites in the latter half of 1954 and early 1955 showed tritium concentrations in the range $3.0–4.2 \times 10^{-18}$ T/H, a value which corresponds with the amount of artificially produced tritium observed in Ottawa rain. Subsurface samples collected at one station off the coast of Nova Scotia in mid-1955 showed an unexpected concentration level and pattern, having a T/H value of 32.4×10^{-18} at the bottom depth of 600 ft., diminishing to a value of 5.4×10^{-18} at the surface. This is not thought to be a result of thermonuclear testing and warrants further investigation.

INTRODUCTION

Discovery of the radioactive nature of tritium in 1939 (1) seemed to eliminate any possibility of the existence of this nuclide in nature. However, in 1946 Libby (6) postulated the production of carbon-14 and tritium by cosmic ray interaction with constituents of the upper atmosphere, and the search for tritium in nature, which had been pursued in the 1930's, was resumed. Natural tritium was finally detected in water by von Grosse, Johnston, Wolfgang, and Libby (4) and in atmospheric hydrogen by Faltings and Harteck (3).

Kaufman and Libby (5) and von Buttlar and Libby (2) have subsequently measured the tritium content of a number of natural water samples. They report Chicago rain-water to have an average T/H ratio of 7.8×10^{-18} during 1953, and find five sea-water samples to range from 0.19 to 1.6×10^{-18} T/H.

Using the same general method as Libby and co-workers, i.e. electrolytic concentration and gas counting, we have measured the tritium content of Ottawa rain-water over the course of several years and have investigated a number of sea-water samples.

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Contribution from Atomic Energy of Canada Limited, Chalk River, Ontario, and Defence Research Chemical Laboratories, Ottawa, Canada. Issued as A.E.C.L. No. 277 and D.R.C.L. No. 207. This paper was presented at the Symposium on Nuclear Chemistry and Radiochemistry held at McGill University, Montreal, Que., September 7–9, 1955.
[2]*Defence Research Chemical Laboratories, Ottawa, Canada.*
[3]*Atomic Energy of Canada Limited, Chalk River, Ontario.*

EXPERIMENTAL

(a) *Isotopic Concentration*

It is necessary to concentrate the tritium in natural water by at least 1000-fold to permit measurement of its radioactivity by conventional counting techniques. The electrolytic process for hydrogen isotope separation is the most attractive for this purpose. The T/H separation factor of ~14 gives a 40% recovery of tritium on simple electrolysis of a sample to 1/10,000 of its original volume. Initially, expecting a T/H ratio of about 10^{-18} or 7.3 disintegrations per minute per liter of water, it was felt that samples of at least one liter were necessary. It was found practical to electrolyze 1 liter down to 50 mgm. in a series of four cells of decreasing size.

These cells are illustrated in Fig. 1. Each cell consists of a glass vessel suitably shaped to maintain a high liquid level around a nickel anode and iron cathode. Foaming and capillary action between the electrodes in the smaller

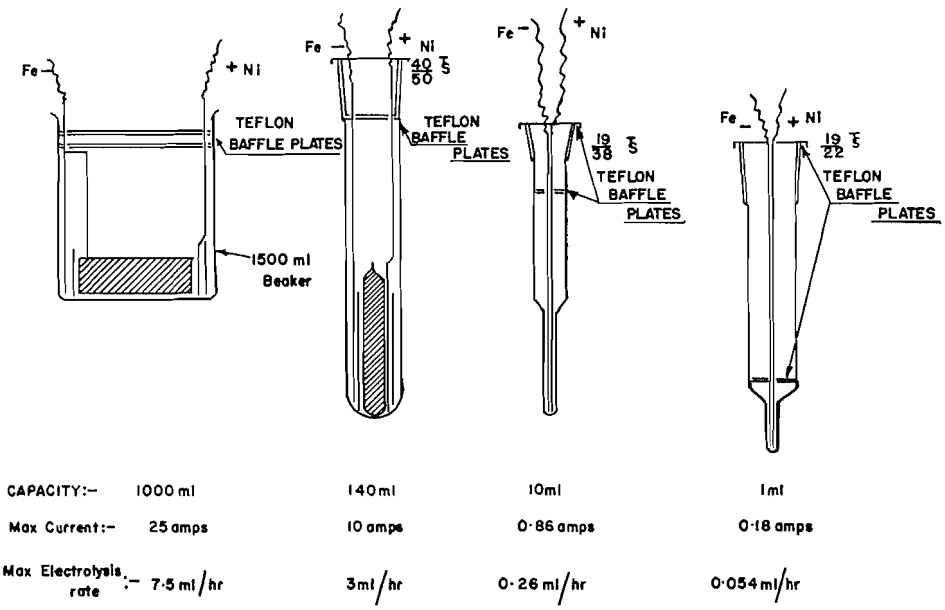

FIG. 1. Electrolysis cells.

cells permit electrolysis at a reasonable rate to a small volume. An initial electrolyte concentration of at least 1% (w/w) potassium hydroxide was found necessary to prevent corrosion of the anode. This limits volume reduction per stage to 10–20 fold, at which point the water is distilled into the next smallest cell, fresh potassium hydroxide added, and the electrolysis continued. Cells are cooled with running water to minimize evaporation losses and improve the separation factor, and current density is limited to 0.5 amp./in.^{2} to prevent local overheating at the electrodes.

Following the suggestion of Kaufman and Libby (5), we have used the

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natural deuterium in all water samples as a convenient tracer for tritium during the electrolytic concentration. It may be readily shown that

$$t/t_0 = (d/d_0)^{\alpha/\beta}$$

where d_0, d, t_0, t denote the initial and final number of moles of deuterium and tritium, and α and β the separation factors of deuterium and tritium, respectively, from protium. Thus, a measurement of the molar recovery of deuterium can be used to calculate the recovery of tritium, knowing the ratio α/β. While α and β are very dependent on experimental conditions they are likely to vary in a similar manner, hence the ratio α/β will be much less variable. In fact, Kaufman and Libby have shown α/β to be relatively constant over wide variations of α. Its value is close to 0.5 and it is sufficient for our purpose to replace the exponential α/β with a square root.

Deuterium analysis of the final concentrate requires only a few milligrams using an infrared spectrometric method developed by Stevens and Thurston (7).

(*b*) *Reduction to Hydrogen*

The remainder of the final concentrate is prepared for counting by conversion to hydrogen with zinc at 375°C. This reduction is rapid and complete, avoiding any isotopic fractionation and minimizing cross-contamination between successive samples. The hydrogen is then passed through a liquid nitrogen trap and introduced into a Geiger counter with 6 cm. argon and 5 cm. ethylene.

(*c*) *Counting*

Samples have been measured in a copper counter, $4\frac{1}{2}$ in. in length, $1\frac{1}{8}$ in. in diameter with a counting volume of 60 ml. defined by polystyrene shields around the central wire extending $\frac{3}{4}$ in. from each copper end plate. Cosmic ray shielding is provided by an annular anticoincidence counter but no further effort has been made to reduce the background below the 3.8 c.p.m. obtained in a 2 in. lead castle.

Good counter plateaus ($\sim$2%/100 v. slope over 300 v.) are obtainable using 6 cm. argon, 5 cm. ethylene, and 0–70 cm. hydrogen provided an electronic quench unit is used in addition to the internal quench gas. The quench unit applies a deadtime of 1200 μsec. to the counter to eliminate double pulses caused by photoemission on arrival of the positive ions at the cathode. The deadtime requirement is dependent on the counter diameter. In the 1 in. counter used in this work the majority of the double pulses occur within a period of 250 μsec., but the longer deadtime gives further improvement at high hydrogen pressures and is no disadvantage at slow counting rates. A 5% drop in counting efficiency, as indicated by an external γ source or a standardized tritium sample, occurs during the first 10 hr. of operation. The counter then becomes stable for an indefinite period and all counting is standardized at this lowered counting efficiency. This drop in efficiency is characteristic of the argon–ethylene mixture in our counting system and is not sensitive to

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the amount of hydrogen present. All counting has been done to $\pm 1\%$ statistical error.

The high hydrogen pressure feasible using the electronic quench unit has allowed the use of a relatively small counter with which a low background is obtainable without extensive effort. An alternative possibility is the elimination of the final stage of concentration and counting in a large volume counter.

RESULTS AND DISCUSSION

(*a*) *Ottawa Rain and Snow, 1951–1953*

The tritium concentrations found in rain and snow samples collected at Ottawa from 1951 to 1954 are presented in Table I. The two samples for 1951 were actually collected at Centre Lake, Petawawa, 100 miles west of Ottawa. All values are corrected for decay back to time of collection of sample.

TABLE I

TRITIUM CONCENTRATION OF OTTAWA RAIN AND SNOW, 1951–1953

Sample No.	Collection date and details	T/H × 10^{18}
80	Jan.–Feb., 1951* Composite snow sample	23.8
74	March 8, 1951* Surface snow sample	39.4
52	Nov. 12, 1952	21.1
66	Aug. 5, 1953	9.4
65	Aug. 23, 1953	28.1
58	Aug. 24, 1953	28.1
59	Sept. 1, 1953	17.1
60	Sept. 16, 1953	36
61	Sept. 21, 1953	38.0
62	Sept. 27, 1953	23.6
63	Oct. 5, 1953	17.7
64	Oct. 14, 1953	19.1
67	Oct. 27–28, 1953	37.8
69	Nov. 11, 1953	42.0
75	Dec. 21, 1953	22.6
Average tritium concentration for 1953		26.6

**Collected from the surface of Centre Lake, Petawawa, 100 miles west of Ottawa.*

There is seen to be considerable variation from sample to sample, but there is no evident correlation with time. The average, unweighted for relative rainfall, of results for the latter half of 1953 is 26.6×10^{-18} and all values, with the exception of one at 9.4×10^{-18} T/H, lie within the range 17–42 $\times 10^{-18}$ T/H. This is about twice the average found by Libby and co-workers for Chicago rain-water of the same period. This may be explained by the fact that most Ottawa rain-water is passed on from the Chicago area and has probably had at least double the exposure to atmospheric tritium since leaving the common oceanic source, namely the Gulf of Mexico.

(*b*) *Ottawa Rain and Snow, 1954*

Tritium values for Ottawa rain-water for 1954, presented in Table II, show marked effects of the thermonuclear tests in the Pacific in the spring of

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TABLE II

TRITIUM CONCENTRATION OF OTTAWA RAIN AND SNOW, 1954

Sample No.	Collection date	T/H × 10^{18}
78	Jan. 13–15, 1954	27.6
418	Mar. 10	2937
419	Mar. 12–14	2118
422	Mar. 25–26	556
427	Apr. 10–11	1287
430	Apr. 20–21	611
435	May 8–9	648
437	May 17	1743
438	May 28–29	855
442	June 10	370
452	July 12	230
460	Aug. 10	159
469	Sept. 10–13	74.4
480	Oct. 9–11	32.1
490	Nov. 13	43.4
499	Dec. 10–12	28.1
513	Jan. 17, 1955	22.3
519	Feb. 15	36.6
527	Mar. 3–4	41.3
Average tritium concentration for 1954		260

that year. Fig. 2 is a plot of these results on a semilogarithmic scale and includes results reported by von Buttlar and Libby (2) for comparison. The tritium concentration is seen to rise in an irregular manner up to 100 times the normal

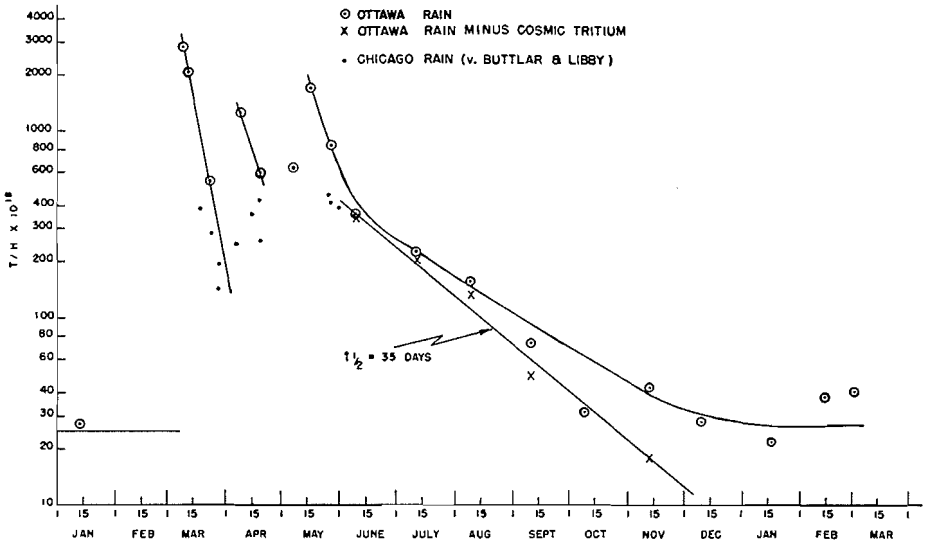

FIG. 2. Tritium content of rain, 1954–55.

level during the months of March, April, and May, then gradually falls back to normal during the summer months, demonstrating a half time for washout of approximately 35 days. The earliest sample collected in March indicates

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that the transport time from the western Pacific to Ottawa was something less than 10 days in this particular case. The lack of major fluctuations after the month of May indicates that the tritium was fairly uniformly distributed by June. This is consistent with meteorological estimates of time required for complete N.–S., E.–W. mixing. The fact that the tritium content of rainfall returned to much the same level as it had been previously indicates that the continued feed-in of artificially produced tritium from the oceans, and perhaps from the stratosphere, is small compared to the rate of production by cosmic processes.

From Fig. 2 we may estimate that the average tritium concentration of the year's rain was 260×10^{-18} T/H, approximately 10 times that of the previous year. At no time was the tritium in Ottawa rain a health hazard, the highest samples analyzed being 1/25,000 of tolerance level.

(*c*) *Surface Sea-water, Late 1954*

Table III presents results for surface sea-water samples collected in the Arctic, Pacific, Caribbean, and Atlantic during the latter half of 1954 and early

TABLE III

TRITIUM CONCENTRATION OF SURFACE SEA-WATER, LATE 1954

Sample No.	Date collected	Locale	Water temp., °F.	T/H $\times 10^{18}$
S1	Aug. 1, 1954	Arctic, 74°N. 91°W.		4.19
S4	Sept. 18, 1954	Arctic, Beaufort Sea		2.98
S2	Oct. 28, 1954	Pacific, west of Mexico		3.58
S3	Nov. 14, 1954	Atlantic, 19°30′N. 64°W.		2.97
S7	Feb. 9, 1955	Atlantic, 50°N. 31°W.	54	3.54
S6	Feb. 10, 1955	Atlantic, 47°N. 47°W.	40	3.60

1955. All results from this widespread series of samples lie in the range $3–4 \times 10^{-18}$ T/H, up a factor of 10 over most of von Buttlar and Libby's 1953 sea-water analyses. If the results for the Ottawa area are taken as representative for the whole northern hemisphere, then the artificially produced tritium deposited on the oceans corresponds to that contained in 1 meter of rain with a T/H ratio of 230×10^{-18}. In the oceans, this would be diluted to a T/H ratio of 3×10^{-18} by mixing to 70 meters. A slightly greater depth of mixing would be required to accommodate runoff from the land areas. Such a depth is consistent with the approximate known limit for rapid mixing of sea-water.

(*d*) *Subsurface Sea-water, 1955*

In an attempt to observe the limit of rapid mixing by tritium analysis, subsurface sea-water samples were taken at two stations, 3–4 miles apart, on the continental shelf about 50 miles southeast of Halifax. At each station the water consisted of two layers of appreciably different temperature and samples were obtained from the bottom, top, and intermediate waters. The rather unexpected results presented in Table IV were obtained. Careful

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TABLE IV

TRITIUM CONCENTRATION OF SUBSURFACE SEA-WATER AT TWO STATIONS, 1955
All samples collected on May 11, 1955

Sample No.	Water temp., °F.	Depth, ft.	T/H × 10^{18}
Station A: 44°17.3′N., 63°15.4′W.; bottom depth 522 ft.			
S13	37	0	10.8
S12	35	261	9.21
S11	46	512	4.56
Station B: 44°18.9′N., 63°09.3′W.; bottom depth 600 ft.			
S10	37	0	5.40
S9	35	300	16.3
S8	46	590	32.4

review of the electrolytic and counting history of these and concurrent samples gives assurance of the validity of the results. Considerable differentiation is observed between samples from the various layers, but not in a manner consistent with the sole feed-in of tritium at the surface. The results suggest that tritium is being fed in at the bottom at Station B, is dispersing towards the surface, but is displaced towards Station A once it crosses the interface between the two layers. This is consistent with the southwesterly movement of surface water in this area. The locale of tritium feed-in at the bottom does not extend to Station A, just a few miles away, and there must be relatively little movement from B towards A on the bottom.

The observation of these high results casts some suspicion on the explanation offered for the level of tritium found in the earlier surface samples. However, the consistency of these results argues in favor of their being the result of a uniform deposition of a large amount of abnormal tritium.

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SOME CUMULATIVE YIELDS OF ISOTOPES FORMED IN THE THERMAL NEUTRON FISSION OF Pu^{239} [1]

By D. M. Wiles,[2] J. A. Petruska,[3] and R. H. Tomlinson

ABSTRACT

The relative yields of the isotopes of cesium, cerium, neodymium, and samarium produced by the thermal neutron fission of Pu^{239} have been determined with a mass spectrometer. Preliminary values of the absolute yields of 16 isotopes of these elements together with four yields of the xenon isotopes have been assigned by means of isotope dilution techniques.

INTRODUCTION

The numerous papers reporting radiochemically determined yields of isotopes formed in the thermal neutron fission of Pu^{239} have been summarized by Steinberg and Freedman (10). Whereas the various values fix the general asymmetric nature of the yield–mass curve, the nature of the fine structure cannot be interpreted from the reported data. Accurate yield data have been reported for the thermal neutron fission of U^{235} (3, 9), and it is therefore of particular interest to obtain accurate fission yield data for other fissionable isotopes, such as Pu^{239}, in order that variations in the yields may be correlated with the nuclear properties of the fissionable isotopes and their products.

The present work reports the relative yields for three isotopes of cesium, three isotopes of cerium, six isotopes of neodymium, and five isotopes of samarium. By means of isotope dilution the number of atoms of each isotope of cesium and neodymium has been determined in a solution of plutonium fission products. From the relative amounts of these fission products, together with some interpolated relative yields, it was possible to normalize the total to 100% and therefore obtain absolute fission yields.

EXPERIMENTAL

A sample of plutonium dioxide (96.1% Pu^{239}) weighing 6 mgm. was sealed in quartz and irradiated for 305 hr. with a flux of 2×10^{13} thermal neutrons per cm.^{2} per sec. in the NRX (Chalk River) Reactor. About 14 months after irradiation the PuO_2 along with most of the fission products was transferred from the quartz capsule into a platinum crucible. The quartz was rinsed with HF so that some of the recoil fission products embedded in the quartz could be obtained. After several successive rinsings with HF and HCl about 80% of the beta and gamma radioactivity was transferred to the platinum crucible. The PuO_2 was converted to the fluoride by evaporation to dryness with HF, dissolved in HCl, and transferred to a polyethylene container. Aliquots of this stock solution were used for mass spectrometric analysis and isotope dilution. For some mass spectrometric analyses the plutonium was separated

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Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario. This paper was presented at the Symposium on Nuclear Chemistry and Radiochemistry held at McGill University, Montreal, Que., September 7–9, 1955.
[2]*Holder of Research Council of Ontario Scholarship 1954–55.*
[3]*Holder of Research Council of Ontario Scholarship 1953–54.*

from the fission products by precipitation with hydrogen peroxide, but it was found that the mass spectra of the fission products could be obtained in the presence of the plutonium, and therefore no separation was used for the second isotope dilution analysis. The details of the isotope dilution and mass spectrometric techniques used for the analysis of fission products have been discussed in previous papers (8, 9).

RESULTS AND DISCUSSION

The observed mass spectrometric data, together with corrections converting the ratios to relative fission yields, are shown in Tables I to IV for the elements cesium, cerium, neodymium, and samarium respectively. Isotope dilution data for cesium and neodymium are also shown in Tables I and III. The evaluated numbers of atoms of Cs^{133} and Nd^{143} per gram of fission product solution, which is shown with the isotope dilution data, give the normalization of the cesium to the neodymium yields which are shown in Table V. The relative yields of masses 140 and 142 given in Table V are obtained from the cerium isotope ratios given in Table II normalized to those of neodymium by means of the 144 mass chain whose yield has been determined with both elements. The relative yields of the samarium isotopes given in Table IV are shown in Table V normalized to those of neodymium in such a manner as to give a smooth curve when the yields are plotted against mass. The xenon

TABLE I

THE RATIOS OF THE CESIUM ISOTOPES OCCURRING IN THE THERMAL NEUTRON FISSION OF Pu^{239} TOGETHER WITH ISOTOPE DILUTION DATA

Isotope	Mass spectrometric ratio	Relative fission yield
Cs^{133}	1.00	1.00
Cs^{135}	0.216±0.001	1.05±0.15*
Cs^{137}	0.962±0.005	0.994±0.005†

Isotope	Ratios after isotope dilution with Cs^{133}		Atoms of fission Cs^{133}/gm. soln. ($\times 10^{14}$)	
	I	II		
	1.127×10^{15} atoms Cs^{133} added/gm. of fission product soln.	0.857×10^{15} atoms Cs^{133} added/gm. of fission product soln.	I	II
Cs^{133}	2.289	1.992		
Cs^{135}	0.216±0.002	0.216±0.002	8.75	8.64
Cs^{137}	0.962±0.006	0.962±0.005	Av. 8.70±0.06	

**Corrected for 3.5 × 10^6 barn neutron absorption cross section of Xe^{135} (8).*
†Corrected for 26.6 year half-life of Cs^{137} (13).

TABLE II

RELATIVE YIELDS OF THE CERIUM ISOTOPES PRODUCED IN THE THERMAL NEUTRON FISSION OF Pu^{239}

Isotope	Mass spectrometric ratio	Relative fission yield
Ce^{140}	1.00	1.00
Ce^{142}	0.90 ±0.01	0.90±0.01
Ce^{144}	0.252±0.005	0.69±0.02*

**Corrected for 282 day half-life of Ce^{144}.*

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yields shown in Table V are the mass spectrometric values given by Fleming and Thode (1) normalized to the cesium isotopes by means of the factor 0.925 ± 0.010 given by these authors for the ratio Xe^{133}/Xe^{134}. The relative

TABLE III

THE RELATIVE YIELDS OF THE NEODYMIUM ISOTOPES OCCURRING IN THE THERMAL NEUTRON FISSION OF Pu^{239} TOGETHER WITH ISOTOPE DILUTION DATA

Isotope	Mass spectrometric ratio	Relative fission yield
Nd^{143}	1.00	1.00*
Nd^{144}	0.558 ± 0.005	0.836 ± 0.006*†
Nd^{145}	0.681 ± 0.005	0.681 ± 0.005
Nd^{146}	0.561 ± 0.005	0.561 ± 0.005
Nd^{148}	0.379 ± 0.002	0.379 ± 0.002
Nd^{150}	0.219 ± 0.002	0.219 ± 0.002

Isotope	Ratios after isotope dilution				Atoms of fission Nd^{143}/gm. of fission product soln. ($\times 10^{15}$)	
	I		II			
	No. of atoms added/gm. of fission product soln.‡ ($\times 10^{15}$)	Mass spectrometric ratio	No. of atoms added/gm. of fission product soln.‡ ($\times 10^{15}$)	Mass spectrometric ratio	I	II
Nd^{142}	0.8559	0.596 ± 0.005	1.794	0.968 ± 0.005	1.051	1.046
Nd^{143}	0.3850	1.000	0.8070	1.000	Av. 1.048 ± 0.003	

*Corrected for 334 barn neutron absorption cross section of Nd^{143} (11).
†Corrected for 282 day half-life of Ce^{144}.
‡Assuming 27.12% Nd^{142} and 12.19% Nd^{143} in natural neodymium (5).

TABLE IV

THE RELATIVE YIELDS OF THE SAMARIUM ISOTOPES PRODUCED IN THE THERMAL NEUTRON FISSION OF Pu^{239}

Isotope	Mass spectrometric ratio	Relative fission yield
Sm^{147}	0.794 ± 0.009	2.79 ± 0.04*
Sm^{149}	1.000	1.79
Sm^{150}	0.790 ± 0.009	—
Sm^{151}	0.932 ± 0.009	1.09 ± 0.02†
Sm^{152}	1.036 ± 0.009	0.881 ± 0.02†
Sm^{154}	0.393 ± 0.009	0.393 ± 0.009

*Corrected for 2.52 year half-life of Pm^{147} (6).
†Corrected for 15,000 barn cross section of Sm^{151} (6).

yields shown in Table V that were not obtained directly in this work have been interpolated from a plot of yield versus mass. The absolute fission yields were obtained by normalizing these relative yields to total 100%.

The accuracy of the relative yields shown in Tables I to IV is probably well represented by the precisions given, although the presence of natural cerium in the fission product solution could have increased the reported relative yield of Ce^{140} without being detected by the methods used. The complete absence of both natural neodymium and samarium, which could be detected by their isotopes which do not occur in fission, seems to indicate that contamination of the cerium is unlikely.

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TABLE V

THE RELATIVE AND ABSOLUTE YIELDS OF SOME ISOTOPES FORMED IN THE THERMAL NEUTRON FISSION OF Pu^{239}

Isotope	Relative yield	Absolute yield, %	Isotope	Relative yield	Absolute yield, %
118–130*	0.900	5.38	Nd^{143}	1.00	5.98
Xe^{131}	0.453	2.71	Nd^{144}, Ce^{144}	0.836	5.00
Xe^{132}	0.632	3.79	Nd^{145}	0.681	4.07
Xe^{133}, Cs^{133}	0.830	4.97	Nd^{146}	0.561	3.36
Xe^{134}	0.898	5.37	Sm^{147}	0.470	2.81
Cs^{135}	0.872	5.22	Nd^{148}	0.379	2.27
Xe^{136}	0.797	4.77	Sm^{149}	0.302	1.81
Cs^{137}	0.825	4.94	Nd^{150}	0.219	1.31
138*	0.900	5.38	Sm^{151}	0.184	1.10
139*	1.110	6.61	Sm^{152}	0.148	0.88
Ce^{140}	1.230	7.36	153*	0.107	0.64
141*	1.160	6.94	Sm^{154}	0.066	0.40
Ce^{142}	1.107	6.62	155*	0.050	0.30
			Totals: This work	74.74%	
			Assumed	25.25%	

Assumed yields.

The relation of the xenon yields to those of the cesium isotopes, as well as the relation of the cerium and samarium isotope yields to those of neodymium, is probably accurate to within 1–2%. The accuracy of the absolute fission yields given in Table V is therefore largely dependent on the isotope dilution of the cesium and neodymium and to a lesser extent on the assumed yields of mass chains whose yields were not determined in this work. The reproducibility of the duplicated (and independent) isotope dilutions carried out for both the cesium and neodymium establishes the relative amounts of each of the isotopes of these elements in the stock solution analyzed. There is, however, some question as to whether this stock solution is representative of plutonium fission products or whether some fractionation of the fission product elements may have occurred. Since only about 80% of the fission product radioactivity was recovered from the quartz irradiation capsule, there may have been some preferential loss of fission products. Attempts to recover all the fission products by dissolution of the capsule were not carried out because of possible contamination which might be present in the quartz. Earlier work had shown that plutonium alloys, which could be dissolved without such losses, introduced large amounts of natural isotope contamination. The irradiation of plutonium dioxide in quartz was therefore specifically adopted in this work in order to minimize such contamination. Although there is no obvious reason why fractionation of the cesium and neodymium would occur with these conditions, further experiments must be carried out in order to establish this point.

The absolute yields given in Table V together with the radiochemically determined yields summarized by Steinberg and Freedman (10) are plotted in Fig. 1. A direct comparison of the two sets of data is difficult in view of the fact that the radiochemical yields only total 93% and the individual values have been considerably altered by the reviewers. Since many of the radio-

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chemical yields were obtained by independent determinations it is not possible to renormalize them as a single group. It is therefore possible that most of the missing 7% of the radiochemical yields may be added in the region of mass 140, in which case, the two sets of data would appear more consistent. In this connection it is worth noting that the radiochemical yields which were deter-

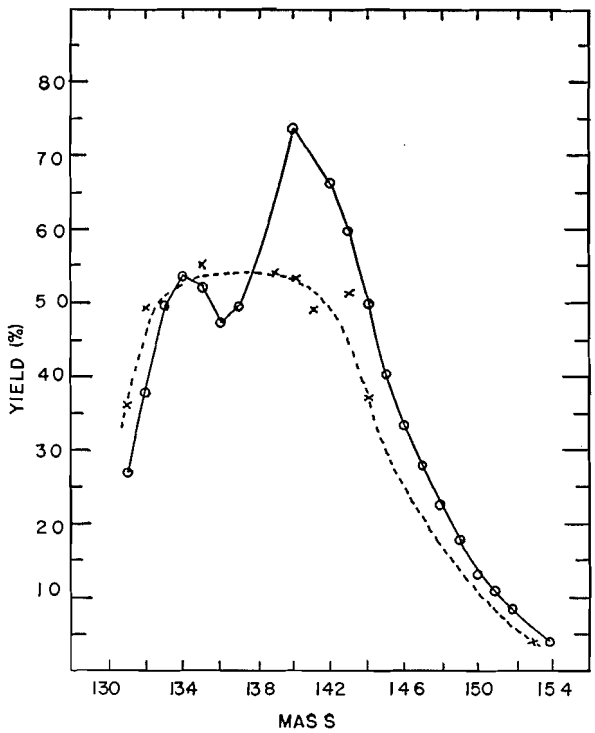

FIG. 1. Thermal neutron fission yields for Pu^{239}.
× Radiochemical ⊙ Isotope dilution

mined during this same period for the thermal neutron fission of U^{235} (10) failed to recognize the now well established fine structure in the region of mass 134.

In Fig. 2 the absolute yields for the thermal neutron fission of Pu^{239} are plotted along with the corresponding yields obtained from the fission of U^{235} (9). It is apparent that the fine structure which is so prominent in the fission of U^{235} is considerably depressed in the fission of Pu^{239}. The presence of fine structure in the U^{235} yield–mass curve has been explained in terms of a structural preference in the primary fission act for nuclides with the 82 neutron configuration (3, 4, 12), as well as various chain branching mechanisms which occur after fission (2, 7, 9). The fine structure of the Pu^{239} yield–mass curve may be qualitatively explained by these same effects.

It is important to note that the present work reports accurate relative yields of the isotopes of cesium, neodymium, samarium, and, to a somewhat lesser degree, those of cerium. The accuracy of the absolute yields can only be

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established after further experiments have determined whether fractionation has occurred in the isotope dilution analysis of cesium and neodymium.

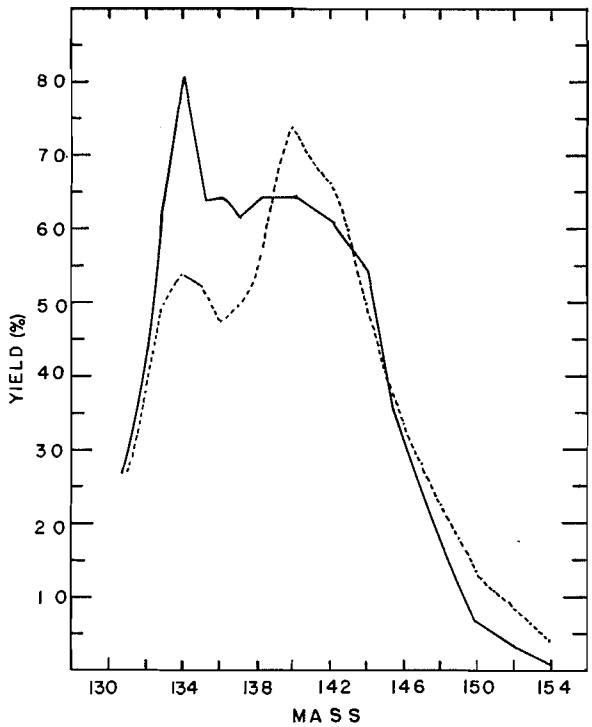

FIG. 2. Comparison of thermal neutron fission yields for Pu^{239} and U^{235}.
-- Pu^{239} — U^{235}

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THE RATIO OF XENON TO KRYPTON IN U^{235} FISSION[1]

By A. T. Blades,[2] W. H. Fleming, and H. G. Thode

ABSTRACT

The ratio of the yield of Kr^{86} to the yield of Xe^{134} in U^{235} fission is $0.257 \pm .005$ determined by isotope dilution techniques. The corresponding yield ratio of total xenon to total krypton in the thermal neutron fission of U^{235} is $5.52 \pm .10$.

INTRODUCTION

An accurate value for the ratio of the quantities of xenon and krypton produced in fission is of considerable interest. Such a knowledge of relative yields in two widely separated mass regions can provide a check on independent absolute fission yield measurements in the light and heavy regions of the mass yield curve.

The relative amounts of the stable and long-lived isotopes of krypton and xenon produced in the neutron fission of U^{235} have been determined in two different ways. Thode and Graham (5), using a mass spectrometer calibrated with standard mixtures of xenon and krypton, obtained a value of 6.2 for the ratio of xenon to krypton in fission. Arrol, Chackett, and Epstein (1) obtained a value of 5.05 for the same ratio by separating the xenon and krypton and measuring their individual volumes. This later value has been considered to be the most reliable and the ratio of xenon to krypton from U^{235} fission has been taken as 5.05.

However, over the past few years the mass spectrometer measurements have been repeated on several occasions and the resulting value for the ratio of xenon to krypton in U^{235} fission has always been considerably higher than the 5.05 value obtained by Arrol, Chackett, and Epstein. For this reason, it was decided to carry out a measurement of the relative quantities of xenon and krypton arising in fission using isotope dilution techniques to eliminate possible errors introduced by mass spectrometer calibrations.

The actual ratio of xenon to krypton in a given uranium sample is a function of the past history of the sample. The relative amount of Xe^{136} in the sample will depend on the conditions under which the sample was irradiated because of the large neutron capture cross section of Xe^{135}. In addition, the amount of 10.27-year Kr^{85} present in the sample will, of course, depend on the age of the material. The remaining xenon and krypton isotopes have half-lives sufficiently short that they are normally not encountered in yield studies dealing with stable end products of the decay chains.

Because of the dependence of the total xenon to total krypton ratio on the above factors, it was more convenient in the present work to measure the relative yields of the two isotopes Kr^{86} and Xe^{134} which are not affected by

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neutron capture processes and the time factor. The ratio of xenon to krypton (totals) is then calculated from the isotope abundances of fission product xenon and fission product krypton reported previously for thermal neutron fission of U^{235} (6). In this later work neutron capture processes and decay factors were taken into account.

EXPERIMENTAL

The determination of the amount of a given element in a particular sample by isotope dilution is carried out in the following manner. There is added to the sample a "spike" consisting of a known amount of the element to be determined but having isotopic composition differing from that in the sample. Separation and purification of the desired element from the sample plus spike is now carried out. From a mass spectrometric analysis of this purified material (sample plus spike) the amount of the element present in the original sample can be calculated if the isotopic constitutions of the sample and spike taken separately are known.

Since all chemical yields up to the point at which the spike is added must be 100%, it is important to add the spike as early as possible in the extraction procedure. Furthermore, complete mixing of the sample and the spike must be assured if accurate results are to be obtained. If these conditions are fulfilled, attainment of 100% yield in subsequent handling is not required.

Xenon and krypton of normal isotopic constitution provide suitable spiking material for the determination of fission product xenon and krypton because the isotopic abundance of the fission product material is radically different from that of the normal material (see Table I).

In order to ensure complete release of the fission product gases from the irradiated uranium metal and thorough admixing of the spike, the following procedure was adopted. The spike consisted of approximately 10^{-8} mole of a mixture of 16.8% krypton and 83.2% xenon prepared by Linde Air Products Company. This was added to about 100 cc. of chlorine gas in a sealed glass and quartz system containing the 0.4 gm. sample of irradiated uranium. The portion of the system containing the uranium metal was heated to 1100°C. for 12 to 24 hr. Under these conditions the uranium reacts completely with the chlorine and, since the chlorides formed are volatile, they distill out of the heated section of the apparatus. This procedure should result in a complete release of the fission gases and efficient mixing with the spike. The excess chlorine and any other gaseous impurities were removed by purification in a calcium furnace. The samples were then analyzed on a conventional 180° mass spectrometer.

RESULTS AND DISCUSSION

A sample of uranium metal irradiated in the NRX reactor was divided into several pieces of approximately 0.4 gm. each. The isotope dilution method described above was used to determine the amounts of xenon and krypton per gram of uranium in six of these pieces.

The isotopic composition of the normal xenon and krypton spike material is

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given in Table I, Column 2. The fission product xenon and krypton isotope abundance data determined on a separate piece of the irradiated uranium to which no spike was added are given in Table I, Column 3.

TABLE I

XENON AND KRYPTON ISOTOPE ABUNDANCE DATA

Isotope	Atom % abundance	
	Spike mixture (normal Xe and Kr)	Fission product sample*
Kr^{78}	0.336	—
Kr^{80}	2.242	—
Kr^{82}	11.34	—
Kr^{83}	11.31	15.23
Kr^{84}	57.44	28.40
Kr^{86}	17.53	56.37
Xe^{124}	0.0910	—
Xe^{126}	0.0855	—
Xe^{128}	1.84	—
Xe^{129}	26.26	—
Xe^{130}	4.03	—
Xe^{131}	21.29	12.07
Xe^{132}	27.14	18.01
Xe^{134}	10.43	33.12
Xe^{136}	8.86	36.80†

**Abundance of stable fission product isotopes only.*
†Not corrected for neutron capture.

The isotope dilution data are summarized in Table II. The precision of each individual determination depends only on the precision of the mass spectrometer measurement which was in general less than ±0.2%. A better measure of the accuracy of the results is the standard deviations of the averages of the six determinations which are about two per cent (see Table II). The fact that the quantities of xenon and krypton per gram of uranium determined for the six samples agree well with each other indicates that both the extraction and

TABLE II

ISOTOPE DILUTION RESULTS

Sample No.	Weight (gm.)	Spike size (10^{-10} moles)	Mass spectrometer ratios		Xe^{131}/gm.U (10^{-10} moles)	Kr^{86}/gm.U (10^{-10} moles)	Kr^{86}/Xe^{134}
			Xe^{129}/Xe^{134}	Kr^{86}/Kr^{84}			
1	0.5856	161.9	0.784	1.553	51.2	13.5	0.264
2	0.3679	161.7	1.037	1.861	52.6	13.7	0.261
3	0.3856	161.5	0.987	1.808	54.5	14.1	0.259
4	0.4277	79.2	*	1.297	54.4	13.7	0.252
5	0.4112	79.0	*	1.315	55.2	13.8	0.250
6	0.4098	162.8	0.986	1.814	51.7	13.2	0.255
				Average	53.3±1.5	13.7±.3	0.257±.005

**The isotope dilution measurement was used to determine the amount of Xe^{131}/gm. for samples 4 and 5. The quantity of Xe^{131}/gm. is calculated from this result and the relative fission product abundance of Xe^{131} and Xe^{134} given in Table I.*

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the mixing of the fission product and spike gases were highly efficient. Actually variations of a few per cent in fission gas content in the different pieces cut from the one uranium sample might be expected because of neutron flux variation in the sample due to self-shielding effects.

The isotope abundances of fission product xenon and krypton reported by Wanless and Thode (6) for samples irradiated in the thermal column (low neutron flux) of the NRX reactor (see Table III) have been corrected for decay

TABLE III

FISSION PRODUCT XENON AND KRYPTON ISOTOPE ABUNDANCE FOR URANIUM IRRADIATED IN THERMAL COLUMN, NRX*

Isotope	Atom % abundance	Absolute fission yield (%)
Kr^{83}	14.10	0.557
Kr^{84}	25.93	1.02
Kr^{85} (10.27 yr.)	7.59	0.300
Kr^{86}	52.38	2.07
Xe^{131}	13.42	2.93
Xe^{132}	20.08	4.38
Xe^{134}	36.91	8.06
Xe^{136}	29.59	6.46

**Fission product isotope abundance from Ref. 6.*

of the 10.27-year Kr^{85} and also for neutron capture by Xe^{135}. Using these data and the Kr^{86} to Xe^{134} ratio of 0.257 from Table II, the calculated ratio for xenon to krypton in thermal neutron fission of U^{235} is $5.52 \pm .10$. This ratio includes Kr^{83}, Kr^{84}, 10.27-year Kr^{85}, Kr^{86}, Xe^{131}, Xe^{132}, Xe^{134}, and Xe^{136} where the Kr^{85} has been corrected for decay and Xe^{136} for neutron capture in Xe^{135}. As stated in the introduction, the actual value of this ratio in a particular sample will depend on the irradiation conditions and decay time of the sample.

The ratio for total xenon to krypton of 5.52 determined in this work is considerably higher than the value 5.05 reported by Arrol, Chackett, and Epstein (1). The discrepancy is actually greater than the above figures indicate since the results reported by the latter workers were not corrected for neutron capture in Xe^{135}. This correction, however, would not be large since the amount of capture in the samples was found to be only 5% of the 136 yield (samples J and K in Ref. 6).

Finally, the absolute yields of the xenon and krypton isotopes given in Table III, Column 3, are obtained by using the xenon and krypton isotope abundances in Column 2, the ratio of Xe^{134} to Kr^{86} from Table II, and an absolute value of 2.93% for Xe^{131} yield. This yield value is based on an absolute yield determination of Xe^{133} by Katcoff and Rubinson (3) and of Cs^{133} by Petruska, Thode, and Tomlinson (4), the two values being 6.62 and 6.59% respectively. A recent determination of the ratio of Xe^{131} to Xe^{133} by Fleming (2) was also used.

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PILE NEUTRON CAPTURE CROSS SECTION OF 33 HR. Ce^{143} [1]

By L. P. Roy[2] and L. Yaffe

ABSTRACT

Ce^{144} has been produced by the successive neutron capture reaction $Ce^{142}(n, \gamma)Ce^{143}(n, \gamma)Ce^{144}$. The pile neutron capture cross section of the 33 hr. Ce^{143} was determined by separating Pr^{144}, the daughter of Ce^{144}, from the rigorously-purified cerium at frequent intervals. The amount of Pr^{144} formed increased linearly with the square of the neutron flux in a manner consistent with that of a successive neutron capture reaction. The value for the pile neutron capture cross section of Ce^{143} was found to be 6.0 ± 0.7 barns.

A. INTRODUCTION

Ce^{143}, a radioactive nuclide with a half-life of 33 hr., is formed as a fission product of uranium and also by the reaction $Ce^{142}(n, \gamma)Ce^{143}$ in a nuclear reactor. A measurement has been made of the pile neutron capture cross section using the activation method. The application of this method to the case of stable nuclides is well known, e.g. Seren *et al.* (13). If a sufficient quantity of a radioactive substance is available, its pile neutron cross section may be measured by the same method, provided only that the radioactivity produced in the activation process may be separated or distinguished from that of the target. This method has been used extensively to determine the cross sections of many transuranic nuclides, e.g. (16), and of certain nuclides which can be prepared and separated readily, e.g. (8).

Unless both the target half-life and the resultant half-life are reasonably long, an experiment of this type necessitates proximity to a nuclear reactor. If the resultant half-life is long the experiment can be done by a second order neutron capture process in which the radioactive target nuclide is continuously generated by neutron capture in a sample of a stable element. This successive neutron capture method has been used to determine the cross sections of many unstable nuclides (1, 2, 3, 7, 9, 11, 15, 17), and higher order neutron capture processes have been used to produce many of the new transuranic nuclides and to determine some of their cross sections (5, 10, 14).

In our case the appropriate stable target is Ce^{142} (11.07% of natural cerium) and the pertinent nuclear reactions are:

$$\begin{array}{ccccc} Ce^{142} & & & & \\ (n, \gamma) & & & & \\ Ce^{143} & \xrightarrow[33\text{ hr.}]{\beta^-} & Pr^{143} & \xrightarrow[13.5\text{ day}]{\beta^-} & Nd^{143}\text{ (stable)} \\ (n, \gamma) & & (n, \gamma) & & (n, \gamma) \\ Ce^{141} & \xrightarrow[280\text{ day}]{\beta^-} & Pr^{141} & \xrightarrow[17.5\text{ min.}]{\beta^-} & Nd^{144}\text{ (stable).} \end{array}$$

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Contribution from the Radiochemistry Laboratory, Department of Chemistry, McGill University, Montreal, Quebec, with financial assistance from the National Research Council of Canada, Atomic Energy of Canada Limited, and the Atomic Energy Control Board. This paper was presented at the Symposium on Nuclear Chemistry and Radiochemistry held at McGill University, Montreal, Que., September 7–9, 1955.

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The 17.5 min. Pr^{144} daughter of Ce^{144} (maximum β-energy = 3.0 Mev.) is very easily identifiable (6). Examination of reactions which take place with the other cerium isotopes shows that only by a second order neutron capture process on Ce^{142} can Pr^{144} be produced.

The relatively short half-life of Pr^{144} enables the determination of the cross section of Ce^{143} to be made without taking into account the cross section of Pr^{143}. This can be done by measuring the Pr^{144} in equilibrium with the Ce^{144} after a suitable decay period. It is much more suitable, from the radiochemical standpoint, to discard the first praseodymium fraction separated, since this will contain some impurities, to purify the cerium and do repeated parent–daughter separations. The relevant differential equations which apply during the irradiation are

$$[1] \qquad dQ/dt = nvP\sigma_0 - \lambda_1 Q - nvQ\sigma_1 \approx nvP\sigma_0 - \lambda_1 Q,$$

$$[2] \qquad dR/dt = nvQ\sigma_1 - \lambda_2 R - nvR\sigma_2 \approx nvQ\sigma_1 - \lambda_2 R$$

where P, Q, and R are the number of atoms of Ce^{142}, Ce^{143}, and Ce^{144} respectively at any time t during the irradiation in a neutron flux nv neutrons/cm.^{2}/sec., and σ_0, σ_1, σ_2 and λ_1, λ_2 are cross sections and disintegration constants respectively. The subscripts 0, 1, 2 refer to Ce^{142}, Ce^{143}, and Ce^{144} respectively.

Assuming P to be constant during the irradiation, and Q and R to be zero at the beginning of the irradiation, the integrated equations at the end of irradiation time T become:

$$[3] \qquad Q_T \approx \frac{nvP\sigma_0}{\lambda_1}(1 - e^{-\lambda_1 T}),$$

$$[4] \qquad R_T \approx \frac{(nv)^2 P\sigma_0\sigma_1}{\lambda_1\lambda_2}(1 - e^{-\lambda_2 T}) - \frac{(nv)^2 P\sigma_0\sigma_1}{\lambda_1(\lambda_1 - \lambda_2)}(e^{-\lambda_2 T} - e^{-\lambda_1 T}).$$

If the sample of cerium is purified from praseodymium at a later time t_1, and the praseodymium allowed to accumulate during a subsequent time t_2, then the amount of Pr^{144} at this time is given by

$$[5] \qquad V = \frac{\lambda_2 R_T}{\lambda_3 - \lambda_2} e^{-\lambda_2 t_1}(e^{-\lambda_2 t_2} - e^{-\lambda_3 t_2})$$

where V is the number of Pr^{144} atoms and λ_3 is the Pr^{144} disintegration constant. R_T is obtained from this equation and σ_1 is then determined by substitution into equation [4].

B. EXPERIMENTAL

Spectroscopically pure samples of cerium oxide, sealed in small quartz ampoules, were irradiated in the NRX nuclear reactor at Chalk River at

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different neutron fluxes for different times. After irradiation, the cerium oxide was removed from the quartz ampoule and dissolved in boiling concentrated sulphuric acid to which 2–3 ml. 30% hydrogen peroxide had been added. The solution was made up to a known volume with distilled water and an aliquot withdrawn. Ten milligrams of lanthanum carrier was added and the rare earths precipitated with concentrated ammonia. The precipitate was dissolved in concentrated nitric acid, cerium was oxidized to the tetravalent state by the addition of solid potassium bromate and precipitated by the addition of a 0.35 *M* solution of potassium iodate. The precipitate was centrifuged, washed twice with a 0.035 *M* solution of potassium iodate, and dissolved in 8 ml. concentrated nitric acid, 0.1 to 0.2 ml. concentrated hydrochloric acid, and a few drops of 30% hydrogen peroxide. Cerium was precipitated from this solution by cautious addition of 12 *M* sodium hydroxide, centrifuged, and washed twice with water. The cerous hydroxide was dissolved in 1 to 2 ml. 6 *M* hydrochloric acid, sulphur dioxide was bubbled through the solution, and the cerium reprecipitated by the addition of ammonia. The above cycle was repeated 8 or 10 times in order to obtain a pure fraction of cerium, free from praseodymium and other rare earths. The cerium was finally converted to the oxalate, filtered, washed with water, ethyl alcohol, ether, and vacuum-dried. The precipitate was weighed as $Ce_2(C_2O_4)_3.10H_2O$.

The oxalate was dissolved in 8–10 ml. concentrated nitric acid, 10 mgm. of lanthanum or praseodymium carrier was added,* and the 17.5 min. Pr^{144} was allowed to grow from the Ce^{144} until equilibrium was established (a few hours). The cerium was oxidized to the tetravalent state by the addition of solid potassium bromate and precipitated as the iodate. The solution, containing the praseodymium, was neutralized with concentrated sodium hydroxide. The praseodymium precipitate was dissolved in concentrated nitric acid, cerium and zirconium carriers added, and an iodate precipitation performed. The praseodymium was precipitated as the hydroxide and the cycle repeated two or three times until a fraction reasonably free from cerium activities was obtained.

The final hydroxide precipitate was transferred as a slurry to an aluminum tray, where it was spread evenly, dried, and the counting-rate determined by a Geiger–Müller counter. The counter was the "end window" type with a mica window of mass 2.3 mgm./cm^2. The counter had previously been calibrated using a 4π-counter. The time of separation varied from 25 to 35 min.

The cerium iodate precipitate was again converted to the oxalate, weighed, dissolved, lanthanum carrier added, and the solution allowed to stand until it was time for another Pr^{144} separation.

C. RESULTS

The decay curves of Pr^{144} were followed for two or three hours, usually through a 221.4 mgm./cm.^{2} aluminum absorber which cut out less energetic

**Both lanthanum and praseodymium carriers were used without any difference being found in the values obtained for σ_1. Pr^{144} was separated from standard Ce^{144} solutions by the use of both lanthanum and praseodymium carriers with identical results. Successive precipitations showed that the removal of activity was complete in either case. Pr^{143} was used as a tracer to determine whether there was any difference in the amount adsorbed by the ceric iodate scavengers if lanthanum and praseodymium carriers were used. Identical results were obtained.*

radiations from impurities. Activities ranging from 100 to 1500 c.p.m. were found with half-lives between 17.0 and 17.5 min. after the subtraction of a small long-lived residual background (2 to 10%). Fig. 1 shows a typical decay curve.

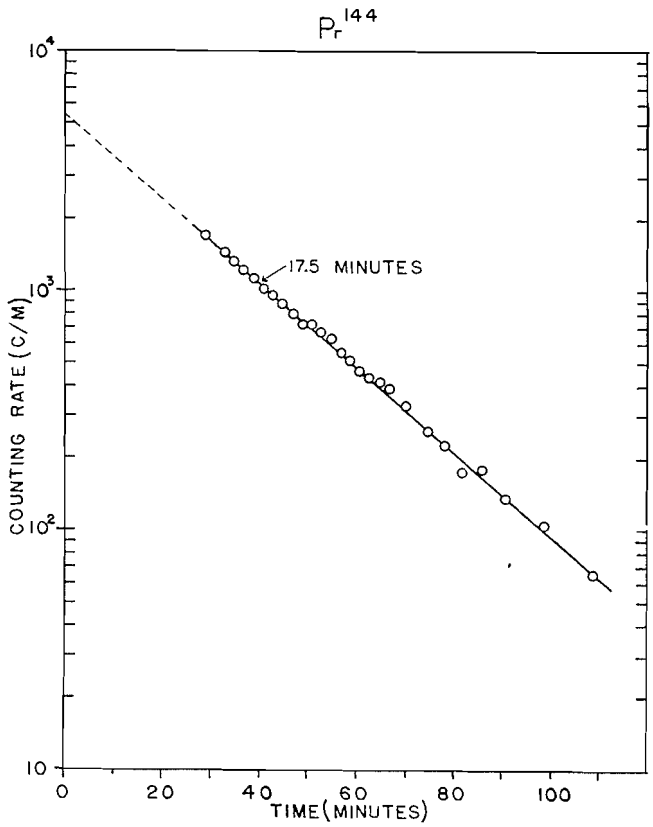

FIG. 1. Decay curve of Pr^{144}. A long-lived background of 35 c.p.m. has been subtracted from the original data to obtain this curve.

The absorption of the Pr^{144} β-radiation in the aluminum absorber was determined in an auxiliary experiment using a pure Ce^{144}–Pr^{144} source separated from fission products and obtained from Atomic Energy of Canada Limited. A correction factor of 1.58 was necessitated by use of the absorber. This agreed with that determined using the Pr^{144} extracted from the irradiated cerium samples.

Pr^{144} was further identified by its absorption characteristics. Decay curves were taken through various aluminum absorbers and the activity in each case was extrapolated to zero time, i.e. the time of separation. The resultant activities were then combined, as shown in Fig. 2, in an absorption curve where the extracted Pr^{144} was compared with the fission-produced Pr^{144}. The results are identical. Using P^{32} as a standard the range of the β-particles

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of Pr^{144} was found to be 1520 mgm./cm.^{2} of aluminum by means of a Feather plot. This works out to a maximum energy of 3.05 Mev. for the β-particles if one uses the Coryell–Glendenin (4) range–energy relationship, in good agreement with spectrometer values (6).

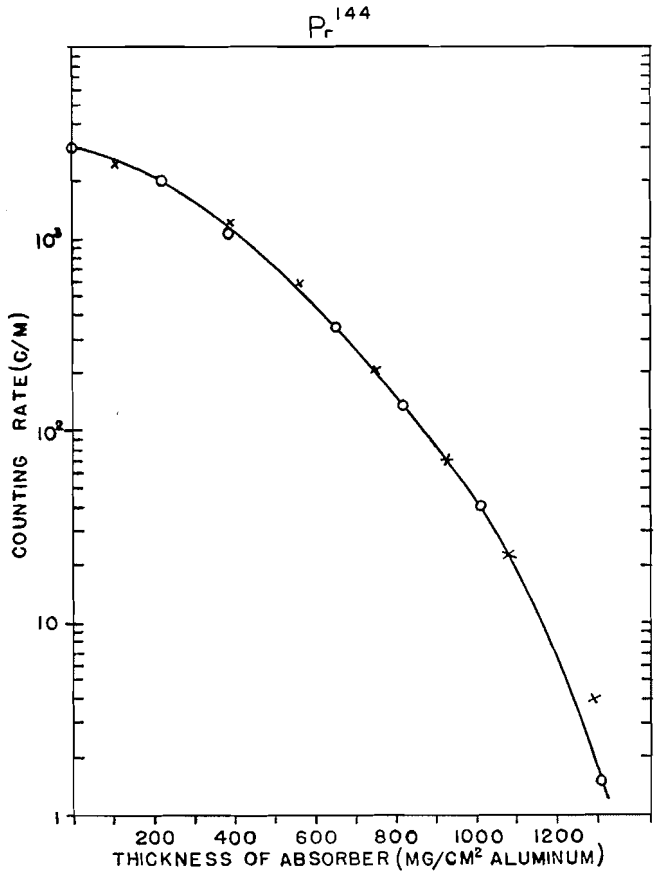

FIG. 2. Absorption curve of Pr^{144} β-radiation in aluminum.
× Pr^{144} obtained from fission products.
○ Pr^{144} obtained in these irradiations.

The results are given in Table I. The disintegration rates of Pr^{144} have been obtained by correcting the observed counting rates, extrapolated to zero time, for chemical recovery, scattering, and absorption of the β-rays before entering the counter, and finally geometrical efficiency of the counter. The neutron fluxes quoted are average values obtained in the same or auxiliary experiments using cobalt as a flux monitor (σCo^{59} = 36.3 barns). The irradiation of the samples was interrupted a number of times by reactor shutdowns. The amounts of Ce^{143} and Ce^{144} formed have been accurately determined by a

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TABLE I

CROSS SECTION OF Ce^{143} OBTAINED BY IRRADIATING Ce^{142} AT DIFFERENT FLUXES FOR DIFFERENT TIMES

Sample No.*	Ce^{142} (atoms $\times 10^{-18}$)	Flux (n./cm.^{2}/sec. $\times 10^{-13}$)	T (sec. $\times 10^{-6}$)	Pr^{144} (dis./sec.)	Ce^{144} (atoms $\times 10^{-10}$)	$\sigma_1 Ce^{143}$ (barns)
1-Pr-1	4.3	7.7	1.295	738	2.78	6.20
1-Pr-2	4.9			951	3.61	7.00
1-Pr-3	6.5			1065	4.60	6.71
1-Pr-4	2.7			411	1.81	6.30
1-Pr-5	21.4			3391	15.67	7.00
1-Pr-6	20.6			3155	14.59	6.73
1-Pr-7	19.6			3202	14.83	7.20
1-Pr-8	18.6			2697	12.50	6.40
1-Pr-9	17.7			2712	12.57	6.76
1-Pr-10	16.9			2620	12.16	6.85
1-Pr-11	16.6			2451	11.39	6.52
1-Pr-12	15.7			2330	10.83	6.56
1-Pr-13	15.0			2202	10.25	6.50
2-Pr-1	12.6	3.8	3.2	1250	5.30	6.30
2-Pr-2	12.8			1110	4.71	5.54
2-Pr-3	12.4			1080	4.58	5.55
2-Pr-4	11.1			1037	4.41	5.95
2-Pr-5	10.3			901	3.83	5.59
2-Pr-6	9.7			871	3.71	5.95
2-Pr-7	13.5			1243	5.37	5.98
2-Pr-8	13.1			1104	4.77	5.46
2-Pr-9	12.4			1225	5.30	6.42
2-Pr-10	11.2			1116	4.83	6.45
2-Pr-11	10.6			1040	4.51	6.38
2-Pr-12	19.5			2019	8.75	6.74
2-Pr-13	19.0			1582	6.87	5.43
3-Pr-1	36.3	5.8	1.58	4230	17.29	6.10
3-Pr-2	35.1			3646	14.87	5.66
3-Pr-3	33.0			3737	15.29	5.92
3-Pr-4	31.4			3489	14.34	5.86
3-Pr-5	30.3			3422	14.08	5.97
3-Pr-6	29.2			3364	13.85	6.06
4-Pr-1	99.2	0.86	2.29	210	0.84	3.57
4-Pr-2	93.6			252	1.01	4.56
4-Pr-3	92.5			237	0.95	4.36
4-Pr-4	90.0			235	0.94	4.43
4-Pr-5	86.4			223	0.90	4.40

**The symbol 1-Pr-4, for example, refers to experiment 1, the 4th repeated extraction of Pr^{144} from Ce^{144}.*

step-by-step application of equations [3] and [4]. Fig. 3 shows the variation of Pr^{144} activity/mgm. Ce^{142} irradiated as a function of irradiation time normalized to one flux value. The linear relationship observed is consistent with a successive neutron capture reaction when the irradiation time is long compared with the half-life of the first order product and short compared with that of the second order product. (This does not prove the above reaction to be second order since, if for example, appreciable uranium impurities were present, the Ce^{144} would be formed as a first order product with the above time–yield relationship.) Fig. 4 shows the variation of Pr^{144} activity/mgm. Ce^{142} irradiated as a function of the square of the neutron flux. The linear relationship observed is consistent with the fact that we are studying a successive neutron capture process.

The average value of the cross section of 33 hr. Ce^{143} was found to be 6.0 ± 0.7 barns, assuming the cross section of Ce^{142} to be 0.95 barns (12). Both of these values are given relatively to $\sigma Co^{59} = 36.3$ barns. The limits shown are the standard deviations. The average value was obtained by weighting the value

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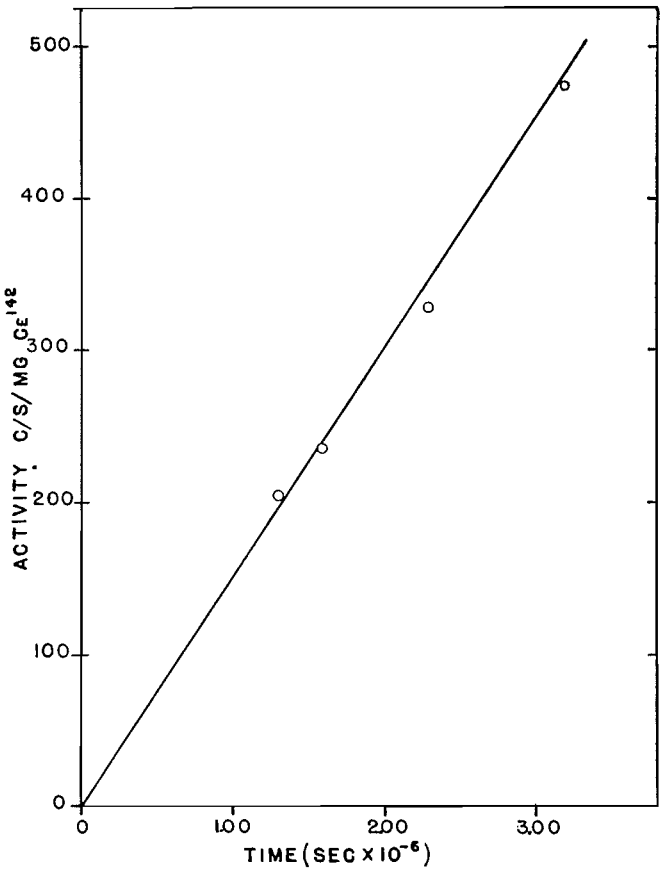

FIG. 3. Variation of Pr^{144} activity/mgm. Ce^{142} irradiated with time of irradiation.

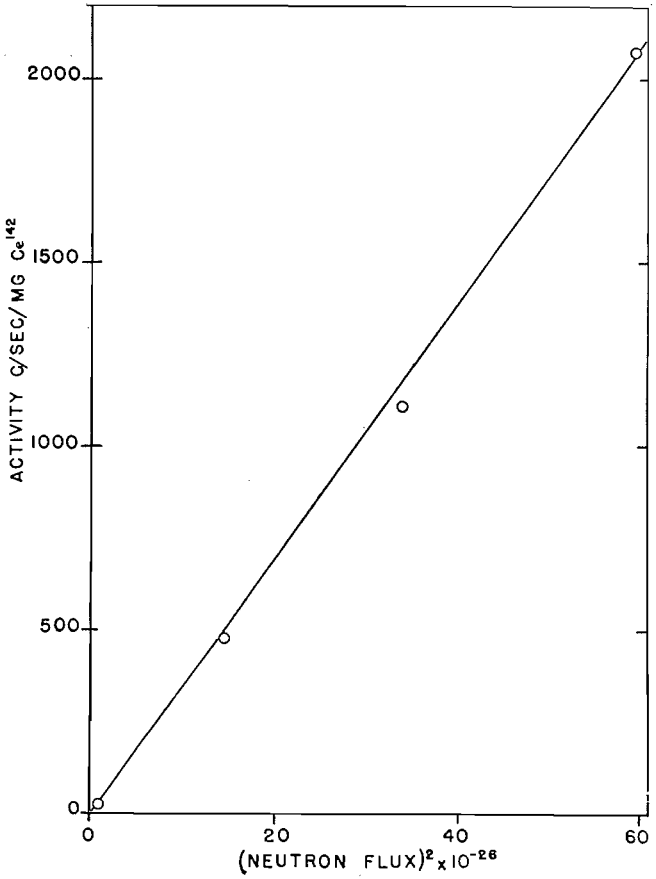

FIG. 4. Variation of Pr^{144} activity/mgm. Ce^{142} irradiated as a function of the square of the neutron flux.

of experiment 4 by the factor 1/3 since this experiment was done at such a low neutron flux.

No experiments were done to determine the epicadmium contribution and the result quoted above should be considered as referring to "pile" rather than "thermal" neutrons.

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THE MASS SPECTROMETRY OF THE ACTINIDE ELEMENTS[1]

By G. R. Hall and A. J. Walter

ABSTRACT

The problems involved in the mass spectrometry of the actinide elements and, in particular, the advantages of using a thermal ionization filament source are discussed. The relative behavior of each of the actinide elements from thorium to americium using this source is described and the results are considered with reference to the Saha equation.

INTRODUCTION

Whilst carrying out the isotopic analysis of large numbers of uranium and plutonium samples using a "solid source" mass spectrometer it has been interesting to observe the relative behavior of these elements in the ionization process. Subsequently a few experiments have been carried out on other elements in the series, i.e. thorium, protactinium, neptunium, and americium, and our aim in this paper is to discuss the results with special regard to the ionization process which occurs.

CONSIDERATION OF ION SOURCES

First it is worth while to review the types of source which might be suitable for isotopic abundance measurements of the heavy elements when high precision and a good sensitivity are required. Normally, unless a double focusing mass spectrometer is to be used, a source which will provide an ion beam with a small spread in ion energy, i.e. less than a volt, is required. This immediately eliminates the gas discharge or hot spark source where large spreads in energy occur, although the ions are produced with high efficiency. Taking into account also the requirement of a very stable ion beam size, then the only suitable source remaining is (1) an electron bombardment source *or* (2) the surface ionization source.

Substances which are either solid with a high vapor pressure or gas under normal conditions may be analyzed using the conventional gas source in which the ions are produced by electron bombardment. In the heavy element series, uranium hexafluoride (b.p. = 56°C.) has often been used and high precision may be attained in measuring the isotopic abundances of the uranium isotopes. Relatively large quantities are required, i.e. in excess of 50 mgm., as much decomposition and reaction of the dissociated and undissociated particles occur at the walls of the mass spectrometer tube. Considerable difficulties can also arise from memory effects. If routine analyses are required and gram quantities of uranium hexafluoride are available, then this source is of great use. No doubt plutonium hexafluoride could also be analyzed in this source but the difficulties would be great. Plutonium hexafluoride has been investigated in some detail (5) and the difficulty in its preparation and especially

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the rapid spontaneous decomposition rate, produced by its own alpha particles, rules out its use in a mass spectrometer source. In addition the use of a highly radioactive gas is not attractive, because of the stringent health precautions which would be necessary. There are no other suitable plutonium compounds which could be used in a gas-type source. It is possible, however, to use this source in conjunction with a crucible which volatilizes materials of high boiling point into the volume of electron bombardment, or, alternatively, to allow the gaseous product to be ionized at a hot metal filament surface. Thus several determinations of the isotopic abundances in natural uranium have been described using such a source, e.g. Nier (6) used samples of UCl_4 or UBr_4, and Palmer (7) has described a source where as little as 1 mgm. of uranium as U_3O_8 may be analyzed. No doubt each of the actinide elements may be analyzed by this method, but once more the main disadvantage is the relatively large size of sample necessary. This is especially so when the material is highly radioactive.

Undoubtedly the most convenient source is the thermal ionization filament source which has been described in the literature by numerous workers. One of the earliest descriptions of such a source was by Dempster (1) who produced positive ions of sodium and calcium from a platinum filament. Later Langmuir investigated electron and positive ion emission from hot filament surfaces and as a result of his work we have the Langmuir–Kingdon modification of the Saha equation [1] which explains the production of positive ions in the thermal ionization source:

$$[1] \qquad (n^+/n_0)\alpha \exp e(W - I)/kT$$

where n^+/n_0 = ratio of positive ions to neutral particles produced by evaporation at the filament surface,

e = electron charge,

W = work function of the filament surface,

I = ionization potential of the particles evaporated,

T = absolute temperature of the filament.

The equation expresses the chance that a particle evaporating from a metal surface will be emitted as a positive ion. It can be seen that a suitable source material is one possessing a low ionization potential and that a metal filament surface possessing a high work function is necessary. Thus, when W is greater than I positive ions are produced with high efficiency. Unfortunately neither of these quantities is usually known sufficiently well for the conditions occurring in a typical mass spectrometer source.

Although the work function for platinum (6.2 v.) is very high, it is necessary to have a filament of higher melting point, especially for the analysis of elements of low volatility. Thus tungsten or tantalum is normally used in heavy element work. The work function of tungsten (4.5 v. for the pure metal surface, *in vacuo*) varies markedly with the surface conditions. Thus for a tungsten surface covered by a monatomic layer of oxygen ions, which can be stable up to ~1800°C., a work function as high as 9.2 v. has been reported (Langmuir and Kingdon, 1925 (4)). As the heavy element is usually deposited

on the filament from nitric acid solution, it is likely that the surface of the filament will become attacked and so an accurate estimate of the work function is impossible.

In the actinide series the ionization potentials are only known for uranium (~4.5 v., an estimate from spectroscopic work), and for plutonium Dr. Dawton at Harwell has recently obtained a value 5.1 v.

These ionization potentials are similar to the possible values for the tungsten surface work function, and hence predictions from the Saha equation of the temperature dependence of positive ion production is difficult. If the ionization potential is greater than the work function of the filament surface (i.e. $I > W$), then the ionization efficiency becomes very small. By taking advantage of the temperature dependence of the Saha equation, however, and operating the filament at a high temperature, the efficiency n^+/n_0 can be considerably increased. Hence a refractory source material is necessary. Unfortunately the advantage to be gained by the increased temperature of the filament is only at the expense of a greatly increased evaporation rate and rapid loss of sample.

Inghram and Hayden (3) have discussed these difficulties and Inghram and Chupka (2) have described a multiple filament source in which the source material is evaporated from one filament at a relatively low temperature to another filament maintained at a very high temperature. It is thus possible to control the sample evaporation rate and yet still to take advantage of the temperature dependence of the Saha equation. This hot filament may be considered to act as a condenser of the particles received from the sample and an almost instantaneous emitter of positively charged ions. The Saha equation is therefore also applicable to this filament. The multiple filament source can produce a great increase in sensitivity for the analysis of small quantities of materials, because it enables a more economic use of the source material.

Thus a disadvantage of the single filament source is that the ions X^+, XO^+, and XO_2^+ are observed and it is not possible to control their formation. In the multiple filament source however, the relative abundance of each type of ion is readily controlled by the temperature of the center filament. It is usually possible to produce mainly X^+ ions and to reduce the number of XO_2^+ ions by a large factor. If the largest ion beam is for oxide ions, and these are measured, then it is necessary to make a correction for the effect of oxygen isotopes, e.g. $[Pu^{239}O^{16}O^{18}]^+$ ions are produced at mass 273, where $[Pu^{241}O^{16}O^{16}]^+$ ions are expected. Hence it is an advantage to measure the X^+ ion beam, where there is no such correction.

In our work with the actinide elements a multiple filament source, similar to that described by Inghram, has been used. The center filament or "hot filament" is of tungsten and is usually maintained at a temperature of 2500°C. or greater, corresponding to a tungsten ion beam of 2×10^{-14} amp. in our instrument. It is probable that we are dealing with a pure tungsten surface at this temperature and the work function can be expected to approach the value 4.5 v. Hence for plutonium we have $I > W$, and so we expect a better

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yield of positive Pu^+ ions for a very hot filament surface. In accordance with these predictions, much larger plutonium ion beams are obtained when a multiple filament source is used than when a single filament source is used, and the size of the Pu^+ ion beam depends directly on the temperature of the center filament.

MASS SPECTROMETER

All the measurements reported below were made with a 60° sector field mass spectrometer with a 6 in. radius analyzing tube. Masses were scanned by varying the magnetic field and the ion current was measured using a vibrating reed electrometer.

MEASUREMENTS ON THE ACTINIDE ELEMENTS

In one series of measurements, a 1 μgm. sample of the actinide element in nitric acid solution was mounted on the sample filament. The solution was evaporated to dryness by passing a small current through the filament. The multiple filament source unit was mounted in the mass spectrometer and the temperature of the center filament was raised quite rapidly to 2500°C., and then the current through the sample filament was slowly increased. The filament currents at which the ions X^+, XO^+, and XO_2^+ were emitted and the variation in beam sizes during the life of the source were noted. After the analysis the multiple filament holder was removed and mounted in a bell jar which was then evacuated. A current was passed through the filaments and their temperatures for the previously recorded filament currents were measured using an optical pyrometer. The temperatures have been corrected for the emissivity of the tungsten surface. Values for the observed ratios X^+/XO^+, when the sample filament temperature was varied from 1000–1850°C., whilst the center filament was maintained at 2500°C., are given in Table I:

TABLE I

VALUES FOR THE RATIO X^+/XO^+ WHEN THE TEMPERATURE OF THE CENTER FILAMENT IS MAINTAINED AT 2500°C., AND THE SAMPLE FILAMENT TEMPERATURE IS VARIED

Ratio	1000°C.	1150°C.	1350°C.	1500°C.	1850°C.
Th^+/ThO^+	ni	ni	Only ThO^+	Only ThO^+	0.05
Pa^+/PaO^+	ni	ni	0.5	1	1
U^+/UO^+	0.2	1	1	1.5	2
Np^+/NpO^+	ni	1.5	4	4	—
Pu^+/PuO^+	ni	60	70	50	35
Am^+/AmO^+	ni	ni	60	100	90

ni = no indication of either X^+ or XO^+.

It is seen that, apart from thorium, it is possible to obtain X^+ ions for isotopic abundance measurements on each of the actinide elements.

As it is very difficult in these experiments to reproduce the exact experimental conditions from filament to filament, a further series of measurements were made in which pairs of the actinide elements (1 μgm. of each in nitric acid solution) were mounted on the sample filament. The results obtained for

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the ratios X^+/U^+ and XO^+/UO^+, respectively, when the sample filament temperature was once more varied, whilst the center filament temperature was maintained at 2500°C., are given in Tables II and III. The filament temperatures were obtained from an optical pyrometer calibration.

Whilst no great precision is claimed for the ratios in Tables I, II, and III, it has usually been possible to reproduce a set of ratios to within a factor of two. The temperature of the center filament is very critical; this effect is discussed later.

TABLE II

VALUES FOR THE RATIO X^+/U^+ WHEN THE TEMPERATURE OF THE SAMPLE FILAMENT IS VARIED

Ratio	1150°C.	1350°C.	1500°C.	1850°C.	2000°C.
Th^+/U^+	No Th^+	No Th^+	No Th^+	0.05	0.1
Pa^+/U^+	No Pa^+	0.06	0.2	—	—
Np^+/U^+	0.2	2	3	—	—
Pu^+/U^+	4	4	4	4	—
Am^+/U^+	No Am^+	3	4	9	—

TABLE III

VALUES FOR THE RATIO XO^+/UO^+ WHEN THE TEMPERATURE OF THE SAMPLE FILAMENT IS VARIED

Ratio	1150°C.	1350°C.	1500°C.	1850°C.	2000°C.
ThO^+/UO^+	No ThO^+	No ThO^+	0.05	0.2	2
PaO^+/UO^+	No PaO^+	No PaO^+	0.1	2	—
NpO^+/UO^+	0.07	0.5	1	—	—
PuO^+/UO^+	0.1	0.1	0.1	0.2	—
AmO^+/UO^+	No AmO^+	No AmO^+	0.1	0.2	—

The main points to be drawn from Tables I–III may be summarized as follows:

(1) In general, increase in temperature of the sample filament, whilst the center filament is at a constant temperature of 2500°C., produces bigger ion intensities, with little change in the ratios. This is to be expected because more particles are being evaporated on to the center filament, but the ionizing conditions remain constant.

(2) As we move across the series from thorium to americium the optimum sample filament temperature is first high, is lowest for uranium, and then rises again for americium. For thorium it is necessary for the sample filament to be at about 1850°C. in order to get a reasonable ion current. Although uranium appears at a slightly lower temperature than neptunium and plutonium the latter appears to produce metal ions more readily. This is in part due to the ratio Pu^+/PuO^+ being so much greater than U^+/UO^+, i.e. a large proportion of the PuO and PuO_2 molecules reaching the center filament are decomposed to Pu^+ and the plutonium sample is therefore used more efficiently.

(3) For thorium, the ions ThO^+ are produced more easily than the Th^+ ions even when the sample filament is at a temperature greater than 1850°C.

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For uranium, the ion beams of U^+ and UO^+ are of similar size, but as we cross the series, the X^+/XO^+ ratio increases until for americium the ratio $Am^+/AmO^+ \simeq 100$. It would appear that the elements become more like gadolinium. Thus, whilst gadolinium produces primarily GdO^+ ions on a single filament, in the multiple filament source Inghram (3) has shown that the Gd^+ ion intensity is much greater than the GdO^+ ion intensity.

(4) It is usually found that, if the currents through the sample and center filaments are held constant for several hours, then the ratio X^+/XO^+ tends to increase. Similar increases in positive ion emission have been described by some of the early workers using filament sources. They are probably due to slow changes in the physical conditions of the tungsten surface, causing a change in work function.

(5) In experiments to determine the relative detection limits for the actinide elements, neptunium, plutonium, and americium appeared to be detected at a lower level than uranium and protactinium. Thorium was the most difficult element to analyze and this must be due, in part, to the refractory nature of the oxide.

(6) Very small samples of the actinide elements may be analyzed in the multiple filament source. Using an electron multiplier collector Tilton (8) has reported a lower limit of 10^{-13} gm. for the detection of uranium.

Several of the ratios which are given in Tables I, II, and III are strongly influenced by changes in the temperature of the center filament. The changes produced in these ratios when the temperature of the center filament is slowly reduced from 2800°C., whilst the sample filament is maintained at a suitable constant temperature, have therefore been investigated. It is found that the ion beams for all the metal ions (X^+) together with ThO^+ and PaO^+ decrease rapidly in size. This would indicate that I is greater than W; for plutonium, as we have seen, this appears to be so. The other monoxide ions behave differently. Thus the UO^+ ion beam remains approximately constant in size until the center filament is at 2200°C., then it decreases rapidly. The PuO^+ and AmO^+ ion beams first increase to a maximum at about 2200°C., and then decrease as the current through the center filament is further reduced.

The dioxide ions PaO_2^+, UO_2^+, and NpO_2^+ resemble the PuO^+ and AmO^+ ions in that the ion intensity increases to a maximum (when the center filament is at 1200°, for the PaO_2^+ ion) and then decreases rapidly. Focusing conditions are such that the dioxide ions which are being detected originate from the center filament. No ions are detected direct from the sample filament. No ThO_2^+ or AmO_2^+ ions are usually observed. The maximum at the relatively low center filament temperature may possibly be explained as follows. There is an initial rise in the ion intensity because the chance that the XO_2 neutral particles can be thermally decomposed to XO and X decreases as the temperature is reduced. Hence there is a greater chance of the XO_2 surviving at the filament surface and being converted to XO_2^+ ions according to the Saha equation. At temperatures below 1800°C. the work function of the tungsten surface may be increased because of the decomposition of the XO_2 molecules by chemical reduction at the tungsten surface and hence the possible formation

of a tungsten oxide film, which may be stable. If the work function then becomes greater than the ionization potential for the particle, then further decrease in the temperature of the filament causes an increase in the ratio n^+/n_0. Finally as the temperature of the center filament drops further, a point will be reached when thermal ionization is no longer possible; hence the final drop at temperatures of about 1000°C.

TABLE IV

VALUES FOR THE RATIOS X^+/U^+ AND X^+/XO^+ WHEN THE TEMPERATURE OF THE SAMPLE FILAMENT IS MAINTAINED AT 1300°C. AND THE CENTER FILAMENT TEMPERATURE IS VARIED

Ratio	2700°C.	2600°C.	2500°C.	2400°C.	2200°C.	2100°C.	2000°C.
Np^+/U^+	—	2	2	2	2	3	4
Pu^+/U^+	—	3	4	6	10	25	—
Am^+/U^+	—	2	3	6	8	28	80
U^+/UO^+	—	1.5	1	0.5	0.3	0.1	—
Np^+/NpO^+	—	4	4	1	—	0.5	0.2
Pu^+/PuO^+	—	70	50	40	20	8	5
Am^+/AmO^+	255	100	60	—	60	27	14

The relative behavior of the actinide elements as the temperature of the center filament is reduced is summarized in Table IV. The ratios for X^+/U^+ and X^+/XO^+ are only intended to indicate a trend of behavior and it should again be emphasized that ratio values are only very approximate. The Np^+/U^+ ratio appears to behave anomalously. Thus, whereas the Np^+ and U^+ ion beams decrease in intensity at about the same rate, the Pu^+ and Am^+ beams appear to decrease more slowly than U^+.

In conclusion it may be said that it is difficult to make predictions from the Saha equation, because, for a rigid application of the equation, it is necessary to include the ionization potential for each of the species under consideration, and these are unknown for the monoxide and dioxide ions and for the metal ions, with the exception of uranium and plutonium. It is possible, however, to explain the results qualitatively using the equation and to obtain a reasonable picture of the ionization process.

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THE PREPARATION AND PROPERTIES OF Pu^{242} [1]

By J. P. Butler, M. Lounsbury, and J. S. Merritt

ABSTRACT

Three samples of plutonium rich in Pu^{242} and containing from 1.7 to 8.6% Pu^{238} have been prepared by the neutron irradiation of Am^{241}. From mass analyses and measurements of the alpha abundance of Pu^{242}, the alpha half-life of Pu^{242} was determined as $3.73 \pm .05 \times 10^5$ yr. The spontaneous fission half-life of Pu^{242} was also measured as $6.6_4 \pm 0.10 \times 10^{10}$ yr.

I. INTRODUCTION

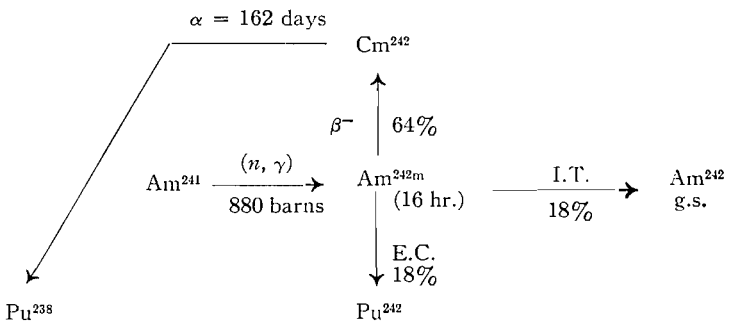
An estimate of about 5×10^5 yr. for the α half-life of Pu^{242} was made by Thompson *et al.* (12) in 1950. Later Asaro (1) reported a value of 9×10^5 yr. for this half-life, based on measurements of the α abundance and mass abundance of Pu^{242} in a sample of plutonium which was mainly Pu^{239}. Asaro determined the α abundance in an alpha-particle spectrograph which employed a 60° symmetrical magnetic analyzer. In a recent paper, Studier and Huizenga (11) summarize data on the spontaneous fission half-lives of the heavy elements, and report a value of 3.8×10^5 yr. for the α half-life and 6.7×10^{10} yr. for the spontaneous fission half-life of Pu^{242}. These values were privately communicated by Mech, and by Ghiorso and Thompson respectively.

In view of the differences and lack of precision in these reported values for the half-life of Pu^{242}, it was considered that a further investigation of this constant would be worth while.

II. PREPARATION OF Pu^{242}

(*a*) *Method*

Samples of plutonium rich in Pu^{242} were prepared by the neutron irradiation of Am^{241}. The nuclear reactions occurring in the neutron irradiation of Am^{241} are as follows (5, 9):



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Am^{241} captures neutrons with an 880 barn cross section (3) to form the excited state of Am^{242}. The metastable state of Am^{242} has an over-all half-life of 16 hr. and decays by three modes: 18% by internal conversion to the ground state of Am^{242}, 64% by β^- decay to Cm^{242}, and 18% by electron capture to Pu^{242}. Since Pu^{242} is formed directly from the 16 hr. Am^{242m} while Pu^{238} is only formed through the intermediate 162 day Cm^{242}, it is clear that in the early stages of an irradiation the growth of Pu^{238} will be slow compared to that of Pu^{242}. Short irradiations followed by rapid separation of plutonium should therefore yield plutonium rich in Pu^{242}.

Quantitative calculations have shown that irradiations of two days would yield samples of Pu^{242}–Pu^{238} containing about 2% Pu^{238}. Plutonium of this composition is necessary for an accurate determination of the half-life of Pu^{242}. Larger amounts of Pu^{238} would make it difficult to measure the α activity of Pu^{242} since the α decay rate of Pu^{242} is about 4000 times slower than that of Pu^{238}. In addition, the α energy of Pu^{242} is less than that of Pu^{238}, so that in an alpha energy spectrogram the small Pu^{242} peak occurs superimposed on the low energy tail of Pu^{238}.

(*b*) *Experimental*

Samples of plutonium containing 98–99 atom % Pu^{242} were prepared by irradiating 50 mgm. of Am^{241} for two days in the N.R.X. nuclear reactor in a neutron flux of 6.5×10^{13} neutrons $cm.^{-2}$ $sec.^{-1}$. The Am^{241} which had been initially freed from all traces of plutonium was irradiated as AmF_3. The fluoride was used rather than the oxide since it had the advantage of being very easily dissolved after the irradiation.

In a two-day irradiation of 50 mgm. of Am^{241} large amounts of α, β, and γ activities are produced: $\alpha = 0.8$ curies, $\beta = 170$ curies, mainly Am^{242m}, and $\gamma = 10$ curies. The γ field of the sample immediately after the irradiation was 10 roentgens at 2 ft. Because of this high radiation field the initial separations were performed remotely in a dry box shielded with 2 in. of lead.

After the irradiation the plutonium was rapidly separated from the americium and curium to prevent further contamination of the Pu^{242} by Pu^{238} which grows in from the α decay of Cm^{242}. The AmF_3 was dissolved in a warm solution of saturated boric acid in 4 *N* nitric acid. The Am, Cm, and Pu were precipitated as hydroxides with NaOH and dissolved in concentrated hydrochloric acid which was 0.1 *N* in nitric acid. This solution was fed onto a Dowex A-1 anion resin column (area 1.1 $cm.^2$, length 6 cm.) which adsorbed the plutonium and allowed the Am, Cm, and most of the fission products to pass through (2). The column was washed with 12 *N* HCl – 0.1 *N* HNO_3 to reduce the amount of Cm held on the column.

The plutonium, which was about 15 μgm. in all, was eluted from the resin column with 1% NH_4I in 12 *N* HCl. The plutonium was reoxidized to Pu^{+4}, and readsorbed on a fresh Dowex A-1 column from which it was eluted with 0.2 *N* HCl. In these steps the plutonium was decontaminated from Am and Cm by a factor of 10^9. The final purification of the plutonium was accomplished by solvent extraction using thenoyltrifluoroacetone in benzene.

III. THE α HALF-LIFE OF Pu^{242}

(*a*) *Method*

From a knowledge of the relative alpha activities and abundances of the plutonium isotopes the half-life of Pu^{242} can be determined from the known half-life of Pu^{238}. For Pu^{242} the equation is as follows:

$$t_{\frac{1}{2}}(Pu^{242}) = \frac{Pu^{238}\text{-}\alpha}{Pu^{242}\text{-}\alpha} \times \frac{\text{atoms } Pu^{242}}{\text{atoms } Pu^{238}} \times t_{\frac{1}{2}}(Pu^{238}).$$

The best value for the half-life of Pu^{238} is 89.6 yr. determined by Jaffey (6).

(*b*) *Experimental*

The samples of plutonium were mass analyzed with a 60°-deflection, 8-in.-radius mass spectrometer with a resolution of 0.3% atomic mass unit (7, 10).

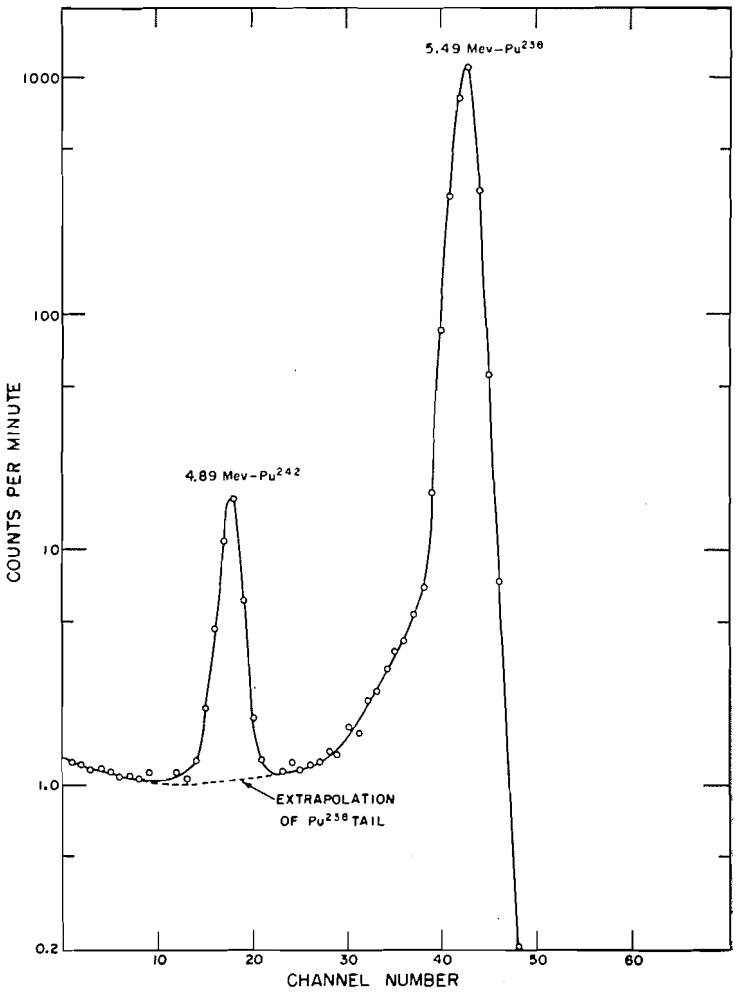

FIG. 1. Alpha spectrum of a sample of Pu^{242}–Pu^{238} containing 1.803 atom % Pu^{238}.

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The surface ionization ion source employed a tantalum ribbon mounted on Kovar terminals. For each analysis a sample of about 15 μgm. of plutonium was used. PuO^+ ions were detected when a current of about 2.5 amp. d-c. was passed through the filament. The mass spectrum was scanned magnetically and the ion current amplified by a vibrating reed electrometer and recorded with a Type G Speedomax. The Pu^{238}/Pu^{242} abundance ratio was calculated from the ratio of the heights of the mass 254 ($Pu^{238}O^{16}$) and mass 258 ($Pu^{242}O^{16}$) ion current peaks. Ten determinations were made of the abundance ratio in each sample and the standard deviation from the mean was $\pm 1\%$. The abundance of Pu^{239} in each of the three samples was low, less than 0.1 atom % in sample 1, and less than 0.01 atom % in samples 2 and 3.

The α pulse analysis of the plutonium was determined with a gridded ion chamber (4) and a 30 channel pulse height analyzer. Thin sources were prepared by vacuum sublimation onto polished platinum disks. The resolution of the chamber was 0.6% full width at half maximum. Fig. 1 shows the alpha spectrum of a mixture of Pu^{238}–Pu^{242} in which the atom per cent of Pu^{238} was 1.8. To determine the α counting ratio of Pu^{238} to Pu^{242} only eight channels over each alpha group were used. In actual practice, to determine the relative abundance of the two alpha groups the same channels were used to obtain the counting rate in each group. This would eliminate errors introduced by differences in channel width. To estimate the α activity of Pu^{242} it was necessary to extrapolate the Pu^{238} α tail under the Pu^{242} peak. Since the Pu^{238} α tail is very flat in the region of 4.9 Mev., there is little uncertainty in this extrapolation. In Table I the reproducibility of the α pulse analysis is shown for a sample of plutonium. The values of the α abundance of Pu^{242} for repeated

TABLE I

REPRODUCIBILITY OF α PULSE ANALYSIS

Sample	Source	α % Pu^{242}
3	A	$1.28_5 \pm 0.01_3$
	A	$1.27_1 \pm 0.01_3$
3	B	$1.27_2 \pm 0.01_2$
	B	$1.29_3 \pm 0.01_3$
3	C	$1.27_2 \pm 0.01_3$
	C	$1.29_8 \pm 0.01_3$
	Average	$1.28_2 \pm 0.009$

counts on three different sublimed sources are listed. The errors quoted are the statistical error in the count plus an error in the extrapolation, about 0.5%. From the results in this table the α abundance of Pu^{242} was determined with a standard deviation of about $\pm 1\%$.

Combining the results of the mass analysis and the α pulse analysis with the known half-life of Pu^{238}, 89.6 yr., the half-life of Pu^{242} was calculated for three samples of plutonium. The results are summarized in Table II.

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TABLE II

HALF-LIFE OF Pu^{242}

Sample	% of Pu^{242}-α's	Atom % Pu^{238}	$t_{\frac{1}{2}} \times 10^5$ yr.
1	$0.26_1 \pm 0.01_2$	$8.62_0 \pm .09_0$	$3.63 \pm .18$
2	$1.38_0 \pm 0.01_2$	$1.69_8 \pm .01_7$	$3.71 \pm .05$
3	$1.28_2 \pm 0.00_9$	$1.80_3 \pm .01_9$	$3.76 \pm .05$
		Weighted average	$= 3.73 \pm .05$

The values of the half-life of Pu^{242} listed in the last column of the table for the three samples agree within the error of the determination. The error for sample 1 (which was prepared by a 9.4 day irradiation of Am^{241}) is larger because the α abundance of Pu^{242} was much smaller and it could not be determined with the same precision as samples 2 and 3.

A weighted average gives a value of $(3.73 \pm 0.05) \times 10^5$ yr. for the α half-life of Pu^{242}. The error quoted is the standard deviation calculated from the experimental results and does not include the uncertainties in the α half-life of Pu^{238} used in the calculations.

IV. SPONTANEOUS FISSION HALF-LIFE OF Pu^{242}

The spontaneous fission half-life of Pu^{242} was determined using plutonium from sample 3 (see Table II). A thin source of about 4 μgm. of plutonium was prepared by electrolyzing a solution of plutonium in 0.3 M ammonium oxalate which was kept slightly acid to phenol red (8). A current density of 150 ma. per $cm.^2$ was used.

The source was fission counted in a simple ionization chamber filled with methane. The chamber was operated at a gas pressure such that both the α-particles and the fission fragments had ranges greater than the spacing between the electrodes. Using an amplifier with a time constant of 10^{-7} sec. the chamber gave good discrimination between α-particles and fission fragments in the presence of 2×10^8 α disintegrations per minute. The background of the chamber was less than 0.5 fission disintegrations per day. The effective geometry of the chamber for a fission source was determined as $96._4\%$ by counting an α source of known disintegration rate at an increased pressure.

The plutonium source which contained 4.05 μgm. of Pu^{242} and 0.0732 μgm. of Pu^{238} gave a spontaneous fission counting rate of 12.3 ± 0.1 disintegrations per hour. When a correction of 2.4% is applied to allow for the spontaneous fission of Pu^{238} ($t_{\frac{1}{2}} = 4.9 \times 10^{10}$ years (11)) a value of $6.6_4 \pm 0.10 \times 10^{10}$ years is obtained for the spontaneous fission half-life of Pu^{242}.

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THE NATURAL ABUNDANCES OF THE URANIUM ISOTOPES[1]

By M. Lounsbury

ABSTRACT

Using a surface-ionization mass spectrometer, the natural U^{238}/U^{235} abundance ratio in uranium obtained from Great Bear Lake Pitchblende has been measured to be 137.80 ± 0.14. From a survey of results reported in the literature on U^{234} a best value of $17{,}325 \pm 550$ was estimated for the natural U^{238}/U^{234} abundance ratio. The corresponding isotopic abundances are 0.7204 ± 0.0007 atom % and 0.00573 ± 0.00018 atom % for U^{235} and U^{234}, respectively.

INTRODUCTION

The first mass spectrographic analysis of uranium was made by Aston (1) in 1931. He observed only U^{238}, and estimated the abundance of other isotopes to total not more than two or three per cent. In 1932, von Grosse (9), from studies of the actinium $(4n + 3)$ series of natural radioactivity, predicted that U^{235} existed in natural uranium to the extent of 0.4 atom %. Dempster (5) in 1935 discovered U^{235} mass spectrographically and determined its abundance to be less than 1 atom %. He also predicted the existence of U^{234} from studies of the uranium $(4n + 2)$ series of natural radioactivity, and calculated that its abundance would be 0.008 atom %, "and therefore too faint to be observed by the mass spectrograph".

Nier (14) in 1939 made the first mass spectrometric analysis of natural uranium and obtained a value of 138.9 ± 1.4 for the U^{238}/U^{235} abundance ratio. Because it was at one time thought that the ratio might be a function of the age of the mineral in which the uranium was found, he measured the ratio for three samples of widely different geologic age. He found that for Swedish Kolm (4×10^8 yr.), Wilberforce Uraninite (1.0×10^9 yr.), and Dakeite (1×10^3 yr.), the ratio was constant to 0.07%, and therefore did not depend on the age of the mineral or its source. Nier also discovered the very rare isotope U^{234}, and determined its abundance to be 0.0059 atom %. Further determinations of the U^{234} abundance have been made by several authors (3, 6, 7, 8, 12) using both mass spectrometric and specific activity methods.

Subsequent mass spectrometric determinations of the U^{238}/U^{235} abundance ratio have been reported by Inghram (11), Fox and Rustad (7), and Chamberlain, Williams, and Yuster (3), all in 1946. Inghram's value of 137.8 was lower than the earlier determination by Nier by almost one per cent. Fox and Rustad actually obtained two values, 137.0 ± 0.7 by electron bombardment ionization, and 138.0 ± 0.3 by thermal ionization. Using the latter ion source they found, as did Nier, that the ratio was constant to 0.03% for two African ores, one Canadian ore, and one Colorado carnotite. Chamberlain *et al.* obtained a value of 139 for the U^{238}/U^{235} ratio, in agreement with the first determination by Nier.

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Contribution from Research Chemistry Branch, Atomic Energy of Canada Limited, Chalk River, Ontario. Issued as A.E.C.L. No. 280. This paper was presented at the Symposium on Nuclear Chemistry and Radiochemistry held at McGill University, Montreal, Que., September 7–9, 1955.

Three estimates of a best value for the U^{238}/U^{235} abundance ratio have been reported in the literature. Bainbridge and Nier (2) in 1950 in their table of isotopic abundances adopted a best value of 139.0 ± 1.4. Fleming *et al.* (6) in 1952 arrived at a best value of 138.0 ± 1.4, a composite of all the determinations, but close to the value of Inghram and the thermal ionization value of Fox and Rustad. In 1953, Hollander, Perlman, and Seaborg (10) in their Table of Isotopes reverted to the 1939 value of Nier.

In view of the difference between the best values of the natural U^{238}/U^{235} abundance ratio, and because of the importance of this ratio in such studies as geologic age determinations and the nuclear processes occurring in reactors fueled with natural uranium, a further investigation of the ratio appeared to be worth while. During the past year and a half, a number of mass spectrometric determinations of the natural U^{238}/U^{235} abundance ratio have been made in this laboratory. The results of these measurements are presented in this paper, along with a comparison of the earlier measurements of U^{234}, in order to estimate a best value for its abundance.

EXPERIMENTAL

A. Uranium Sample

The uranium sample used in this investigation was obtained from Pitchblende from the Eldorado mine at Port Radium on Great Bear Lake in northern Canada. The age of the Pitchblende has been determined by Collins, Farquhar, and Russell (4) to be 1400 ± 50 million years. A highly purified sample of $UO_2(NO_3)_2.6H_2O$ was prepared* and dissolved in 1 *N* HNO_3 to give a solution with a concentration of 5 mgm. U/ml., from which 3λ aliquots were taken for mass analysis.

B. Mass Spectrometry

A 60°-deflection, 8-in.-radius mass spectrometer (13) with a mass resolution of 0.3% was used for this work. The thermionic emission ion source employed a tantalum ribbon filament (0.001 in. × 0.030 in. × 0.250 in.) mounted on pickled Kovar terminals (Stupakoff No. 9807). Fifteen micrograms of uranium contained in 3 microliters of the stock solution was dried on the filament by passing a current of about 1 amp. through it in air.

The loaded filament was mounted in the ion source and by differential pumping the mass spectrometer tube was evacuated to about 2×10^{-7} mm. Hg as indicated by the ionization gauge. UO_2^+ ions were detected when a current of 2.0 to 2.5 amp. d-c. was passed through the filament. The ions were accelerated to 6,000 to 10,000 volts energy, collimated in a beam, and separated according to mass in a magnetic field of 9,000 to 12,000 gauss. The mass spectrum was scanned magnetically, and the ion current was amplified by a Vibrating Reed Electrometer (Applied Physics Corporation, Model 30) with a 2×10^{11} ohm input resistor. The output from the amplifier was fed through a calibrated attenuator system to a fast (0.8 sec. full-scale response) Speedo-

*The author is deeply indebted to Professor L. Yaffe, McGill University, Montreal, for supplying the purified sample of uranyl nitrate.

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max Recorder (Type G). The mass spectrum was scanned slowly (10 sec. per peak) and continuously in the direction of increasing and decreasing mass alternately.

RESULTS AND DISCUSSION

At the relatively low ion source filament temperatures used in this work, the predominant ion emission was UO_2^+, with a very small emission of UO^+ ions. In the recorded mass spectrograms, ion current peaks were observed at the mass numbers shown in Table I. The peak at mass number 266, due to

TABLE I

IONIC SPECIES IN UO_2^+ MASS SPECTRUM

Mass No.	Ionic species
266	$U^{234}O^{16}O^{16}$
267	$U^{235}O^{16}O^{16} + U^{234}O^{16}O^{17}$
270	$U^{238}O^{16}O^{16}$
271	$U^{238}O^{16}O^{17}$
272	$U^{238}O^{16}O^{18} + U^{238}O^{17}O^{17}$

the very rare $U^{234}O^{16}O^{16}$ combination, was observed only if the total ion current was increased by operating the filament at a temperature above the optimum value for long sample life. Therefore the $U^{234}O^{16}O^{17}$ combination made a negligible contribution to the height of the mass 267 peak, and the U^{238}/U^{235} abundance ratio was calculated directly from the ratio of the heights of the mass 270 ($U^{238}O^{16}O^{16}$) and the mass 267 ($U^{235}O^{16}O^{16}$) ion current peaks.

The results obtained from the recorded mass spectrograms are presented in Table II. Each of the 11 determinations listed is the average obtained from 20 or more spectrograms. The error quoted in each case is the standard devi-

TABLE II

ISOTOPIC ABUNDANCE OF U^{235}

Obs. No.	U^{238}/U^{235}	Atom % U^{235}
1	137.84±0.19	0.7202±0.0010
2	138.02±0.11	0.7193±0.0006
3	137.91±0.11	0.7198±0.0006
4	137.74±0.11	0.7207±0.0006
5	137.62±0.15	0.7214±0.0008
6	137.95±0.25	0.7196±0.0013
7	137.81±0.20	0.7204±0.0010
8	137.81±0.18	0.7204±0.0009
9	137.66±0.10	0.7211±0.0005
10	137.92±0.10	0.7198±0.0005
11	137.56±0.14	0.7217±0.0007
Grand mean	137.80	0.7204
S.D.	±0.14	±0.0007

ation of the mean. The grand mean is the average of the 11 determinations with equal weight assigned to each of them. The error attached to the grand

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mean is the standard deviation of the 11 determinations from it. Possible systematic errors which could affect the accuracy of the grand mean are: (*a*) isotopic fractionation in the vaporization process, (*b*) mass discrimination in the ionization process, (*c*) magnetic mass discrimination in the ion source, (*d*) electrostatic mass discrimination in the source, (*e*) magnetic mass discrimination in the analyzer, and (*f*) non-linearity in ion-current measurements.

Isotopic fractionation in the vaporization process could arise from possible preferential evaporation of the lighter $U^{235}O^{16}O^{16}$ molecule, caused by its higher thermal velocity, relative to $U^{238}O^{16}O^{16}$. If evaporation of the sample occurred from the liquid phase and there was perfect mixing at the surface of the liquid, isotopic fractionation could occur and cause a maximum change in the U^{238}/U^{235} abundance ratio of 0.5%, equal to the square root of the ratio of the masses 270/267. With the refractory oxide of uranium, evaporation is from the solid phase, and therefore mixing at the surface of the solid and isotopic fractionation should be negligible. To prove this, abundance ratios were measured from the time emission began until the sample was completely evaporated from the filament. If there were any isotopic fractionation, the U^{238}/U^{235} abundance ratio would increase with time. No such effect was detected.

Mass discrimination in the ionization process would occur if the ionization efficiency was a function of the isotopic mass. However for the thermal process, the ionization efficiency is a function of the ionization potential and not of the mass, and therefore this effect is negligible.

Magnetic mass discrimination could not occur in the ion source because the thermal source required no magnetic field as does a bombardment source with an electron focusing magnet.

There was no electrostatic mass discrimination in the ion source because the ion energy was held constant and the mass spectrum scanned magnetically. If the spectrum had been scanned electrostatically, the higher accelerating potential required to bring the lighter $U^{235}O^{16}O^{16}$ ion to focus on the collector would have resulted in increased ion source efficiency for the lighter ion, and caused the U^{238}/U^{235} ratio to be too low.

With magnetic scanning of the mass spectrum, the ion paths of $U^{235}O^{16}O^{16}$ and $U^{238}O^{16}O^{16}$ through the mass spectrometer tube are identical, and thus the condition for no discrimination in the analyzer is fulfilled.

Inaccuracy in measurements of the abundance ratio could be caused by non-ohmic response of input resistor of the vibrating reed electrometer, or by non-linearity of response of the electrometer and recording system. The input resistor showed no evidence of non-linearity in the range from 0.006 to 2 volts used in these experiments. Similarly the electrometer and recorder gave no evidence of non-linear response over a 10-fold range in total ion current. The measured U^{238}/U^{235} abundance ratio was completely independent of the magnitude of the ion current.

Therefore it is concluded that the various systematic errors discussed above either were not present, or were not greater than $\pm 0.1\%$, the standard deviation from the grand mean, and to this degree of accuracy, the measured ion current peak heights were proportional to isotopic abundances.

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The value obtained for the U^{238}/U^{235} abundance ratio in uranium from Great Bear Lake Pitchblende was 137.80 ± 0.14. Because Nier (14) and Fox and Rustad (7) have shown that the ratio is independent of the age or the source of the mineral from which the uranium was obtained, the value of 137.80 ± 0.14 obtained for the ratio in this work, which is in agreement with the determination by Inghram (11), may be assumed to apply to all natural uranium. A summary of the various published values of the U^{238}/U^{235} ratio is given in Table III.

TABLE III

ISOTOPIC ABUNDANCE OF U^{235}

Author	Reference	Method	U^{238}/U^{235}
Nier, 1939	14	El. bomb.	138.9 ± 1.4
Inghram, 1946	11	Thermal	137.8
Fox *et al.*, 1946	7	El. bomb.	137.0 ± 0.7
Fox *et al.*, 1946	7	Thermal	138.0 ± 0.3
Chamberlain, 1946	3	El. bomb.	139
Bainbridge *et al.*, 1950	2	Best value	139.0 ± 1.4
Fleming *et al.*, 1952	6	Best value	138.0 ± 1.4
Hollander *et al.*, 1953	10	Best value	139.0 ± 1.4
This paper, 1955		Thermal	137.80 ± 0.14

Six values of the U^{234} abundance, ranging from 0.00504 to 0.00591 atom %, have been reported in the literature (3, 6, 7, 8, 12, 14) as shown in Table IV. A best value is rather difficult to arrive at, because several authors, claiming

TABLE IV

ISOTOPIC ABUNDANCE OF U^{234}

Author	Reference	Atom % U^{234}
Nier, 1939	14	0.00591 ± 0.00059
Fox *et al.*, 1946	7	0.00555 ± 0.00017
Chamberlain *et al.*, 1946	3	0.00504 ± 0.00030
Goldin *et al.*, 1949	8	0.00590 ± 0.00008
Kienberger, 1949	12	0.00557 ± 0.00006
Fleming *et al.*, 1952	6	0.00545 ± 0.00004
Best value		0.00573 ± 0.00018

1% accuracy, differ from each other by about 10%. The first three values listed were obtained by the mass spectrometric method. The value of Chamberlain *et al.* (3) appears to be too low because the value of the half-life of U^{234} determined using their abundance of U^{234} is about 10% too low. The values of Nier (14) and Fox and Rustad (7) agree well within the quoted limits of error. Goldin *et al.* (8) calculated their value from the specific alpha-activity of pure U^{234} and U^{238}, using Nier's value for the U^{238}/U^{235} abundance ratio. The method required many operations subject to error, but the result is in remarkable agreement with the value of Nier. Kienberger's (12) value is based on specific alpha-activity and mass spectrometer analyses of samples of uranium highly enriched in U^{234}, and on the specific alpha-activities of U^{238} and natural urani-

um. The value thus calculated is in excellent agreement with the value of Fox and Rustad, but is significantly different from that of Goldin *et al.*, considering the low limits of error imposed on these two values. Fleming *et al.* (6) based their determination on the specific alpha-activity of natural uranium and of U^{234}. The value thus obtained is in agreement with the value of Fox and Rustad within the quoted limits of error.

Thus, excluding the value of Chamberlain *et al.* for the reason discussed above, the values obtained for the natural abundance of U^{234} fall into two groups, one giving 0.0055 atom %, and the other giving 0.0059 atom %. A best value of 0.00573 ± 0.00018 atom % is estimated to cover the most probable limits of the range.

Using the value of the U^{235} abundance obtained from this work, and the best value of the U^{234} abundance estimated from the survey of the literature, the natural abundances of the uranium isotopes are as given in Table V.

TABLE V

NATURAL ABUNDANCES OF THE URANIUM ISOTOPES

Mass No.	Abundance (atom %)
234	0.0057 ± 0.0002
235	0.7204 ± 0.0007
238	99.2739 ± 0.0007
	$U^{238}/U^{234} = 17{,}325 \pm 550$
	$U^{238}/U^{235} = 137.80 \pm 0.14$

ACKNOWLEDGMENT

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DISINTEGRATION-RATE DETERMINATION BY 4π-COUNTING

PART IV. SELF-ABSORPTION CORRECTION: GENERAL METHOD AND APPLICATION TO Ni^{63} β-RADIATION[1]

By B. D. Pate[2] and L. Yaffe

ABSTRACT

A method of preparing thin uniform sources of radioactive materials for use in a 4π counter is described. The radioactive nuclides are formed into organic compounds and are subsequently distilled on to thin VYNS films. Electron microscope photographs of the deposits are shown. The material is uniformly deposited in crystals of about 1 μ in diameter. The distillation can be rendered quantitative. The amount of material on the film can be estimated either spectrophotometrically *in situ* or by appropriate chemical means. Using this method a self-absorption curve for Ni^{63} (maximum beta energy 67 kev.) is obtained.

A. INTRODUCTION

In previous publications (15, 16, 17, 18) we have discussed the principles of 4π-counting and the errors to which disintegration-rate determinations by this method are subject. We have shown that the error from departure of the counter response probability from a value of unity can be reduced to less than 0.1% and that arising from absorption of radiation in the source-mount can be reduced to less than 0.2% of the source disintegration-rate, for beta-emitters of end-point energy down to 67 kev. Similar results were obtained for emitters of other forms of radiation. This paper will describe methods for correcting for the remaining source of error: absorption of radiation in the material of the source itself.

Owing in part to the recent advances in technique for correcting for other errors, self-absorption is at present and appears likely to remain for some time the factor limiting the accuracy of 4π-counting, and indeed all disintegration-rate determination methods involving solid sources (with the possible exception of coincidence counting).

Self-absorption effects become more important as the radiation energy is reduced, and in the 4π-counting system are generally much greater than in systems of smaller counting geometry owing to the ineffectiveness of self-scattering processes (1, 2, 3, 7, 14, 24). However very little systematic work on self-absorption by experimenters using 4π-counters has been reported.

Meyer-Schützmeister and Vincent (12) were aware of the significance of self-absorption in S^{35} sources however. Their method of source mounting (vacuum evaporation or "freeze-drying" of solutions) produced crystals of 2–3 μ in diameter. If the material was deposited so as to be concentrated into one crystal of 20 μ diameter, the apparent activity was observed to be lower by 30%. In order to allow for self-absorption, these authors assumed the

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[2]*Holder of a National Research Council Studentship.*

crystals to be spherical in shape, and computed radiation absorption using an absorption coefficient value from external absorption measurements and assuming the absorption to be exponential.

However when this method of source preparation is used with thin films (5–10 μgm./cm.^{2}) numerous tears are produced in the film, owing probably to the rapid expansion of the droplet under the conditions of rapid evaporation.

Hawkings *et al.* (5) proposed a better method of correcting for, or rather ensuring the absence of, significant absorption effects. Their procedure was the progressive dilution of the stock solution from which sources were prepared until a constant specific activity (after correction for the dilution) was observed. Alternatively a plot of the logarithm of the counting-rate against the aliquot used could be extrapolated to infinite dilution. This method, applicable in general to high specific activity materials only, is however not infallible. Material from dilute solution will, unless elaborate precautions are taken, still crystallize into local aggregates, and even with such precautions, crystal size cannot be reduced indefinitely. Thus self-absorption may still be significant in residues from evaporation which are invisible, and further dilution will not necessarily lead to a true disintegration rate figure.

A recent paper by Seliger and Schwebel (22) emphasizes the importance of the method of source preparation. Different methods of mounting Sr^{90} were found to give sources differing in counting-rate by 5%, and similar but larger effects were found for Co^{60}, mounted by evaporation of a solution with and without prior precipitation by ammonia. Micrographic examination of even the best residues showed clumping of source material. No systematic attempt was made to determine and correct for absorption losses, such corrections as were made being mostly quite arbitrary.

Thus the subject of the determination of and correction for self-absorption in the 4π-counter is virtually untouched. The problem of making such a correction in a precise way divides itself into two parts,

(*a*) the preparation of samples of radioactive material in which self-absorption effects are minimal, uniform, and reproducible and

(*b*) the determination of the extent of self-absorption in the sample so prepared as a function of its superficial density, and consequent correction of the observed disintegration-rate.

B. EXPERIMENTAL TECHNIQUES AND RESULTS

(*a*) *Source Preparation*

The methods of sample mounting used in conventional counter systems, involving manipulations of material in the solid state, are not suitable for the most accurate work with a 4π-counter. This follows from the use of very thin and comparatively fragile plastic films for the source mount, described elsewhere (16). Handling of solids in the form of slurries is likewise unsatisfactory since these tend to form large aggregates, or tear the film on drying.

The usual method of mounting 4π-counter sources then is by drying a suitable aliquot of a stock solution (5, 12, 20). However, as mentioned above, such an evaporation procedure will usually lead to local agglomerates of crystals (most often at the periphery or near the center of the original drop)

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rather than to an even layer of material. This is especially the case when the source-mounting film is particularly hydrophobic, like VYNS, as is seen in Fig. 1, a photomicrograph of a sodium sulphate deposit (~100 μgm./cm.²) produced by this method. Under these conditions self-absorption effects will be neither minimal nor reproducible.

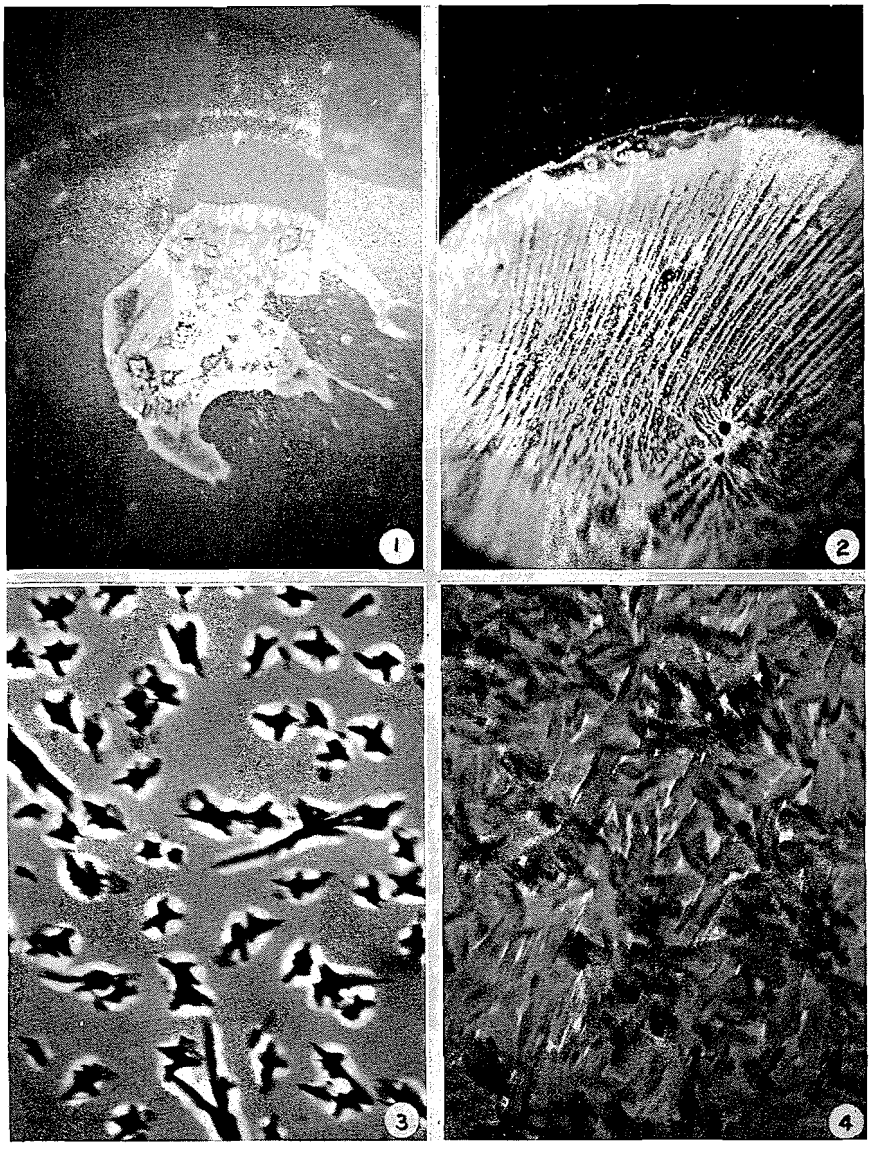

FIG. 1. Photomicrograph (×20) of deposit from the evaporation of Na_2SO_4 solution under infrared irradiation on 5 μgm./cm.² VYNS without insulin.

FIG. 2. Photomicrograph (×20) of deposit from the evaporation of Na_2SO_4 solution under infrared irradiation on 5 μgm./cm.² VYNS film after wetting film with 5% insulin solution.

FIG. 3. Electron micrograph (×10⁴) of a deposit of cobalt 1-nitroso-2-naphthol on VYNS film produced by vacuum distillation. Deposit superficial density 1.2 μgm./cm².

FIG. 4. Electron micrograph (×10⁴) of a deposit of nickel dimethylglyoxime on VYNS film produced by vacuum distillation. Deposit superficial density 5 μgm./cm².

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A more evenly spread deposit is obtained (9) if the surface of the film is rendered hydrophylic, e.g. by treatment with a solution of a protein such as albumen or insulin (10, 11). Under these conditions the deposit is distributed over a wider area, and is more uniform in a macro sense. This is clearly seen in Fig. 2, a photomicrograph of a sodium sulphate deposit ($\sim$100 μgm./cm.^{2}) produced after insulin treatment of the film. However the actual crystal sizes obtained are still quite large and very variable (several millimeters long and 30 to 100 μ in diameter). The disadvantages of methods involving the freeze drying of solutions have already been discussed.

An improved method of source preparation is therefore desirable, particularly for use with very low energy particle emitters, and we find the vacuum distillation of solid source material directly on to the film, using compounds with large organic groupings, to be a suitable procedure. As a method of producing thin even layers of metals and salts, this procedure is of course both of long standing and of widespread employment (8). Its use in this laboratory to coat VYNS source-mounting films with gold has already been described (15). Further it has already been used to mount radioactive materials both for beta-spectrometry (10, 19) and in 4π-counters (6, 21). However no regular use of it nor any attempt to employ it in the present way for self-absorption studies has been reported.

The distillation apparatus used by us is shown diagrammatically in Fig. 5. The furnace consists of a vacuum jacket of pyrex glass containing a platinum crucible A. This contains a charge C of radioactive material to be distilled, and is heated by means of a radio-frequency generator and work-coil B. This coil consists of 12 turns of number 20 gauge copper wire, coated with

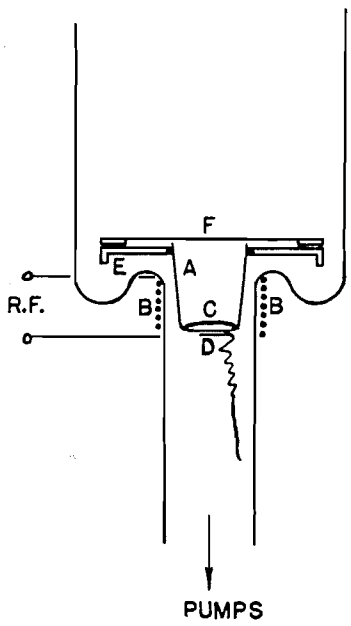

FIG. 5. Vacuum distillation furnace (diagrammatic).

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teflon in order that the insulation between turns might be unaffected by heating (by radiation from the interior of the furnace) to 200° to 300°C.* The crucible temperature is measured by means of a Chromel–Alumel thermocouple D and millivoltmeter.

The crucible is supported by an aluminum mount E, from which it is however thermally insulated by means of a mica ring. The mount allows the source-mounting gold-coated VYNS film to be positioned accurately 0.5 mm. from the mouth of the crucible. The lower end of the furnace is connected, via two traps in series cooled with liquid nitrogen to remove any activities carried in the gas phase, to a rotary pump capable of maintaining a pressure in the apparatus of 0.1 μ Hg. The exhaust from the pumping system was finally vented into the fume hood as a further precaution. Controlled crucible temperatures up to 1000°C. are at present attainable, and a 10 μgm./cm.^{2} VYNS mounting film shows no sign of deterioration in proximity to the hot crucible under vacuum for 10 min. The crucible is cooled very nearly to room temperature before the system is opened, by venting a small air leak above the furnace and allowing air to be pumped past the hot surfaces. It is found that with this design of furnace, transfer of material from the crucible to the film is very nearly 100% quantitative.

Of the materials that can successfully be distilled with the temperature range and pressure at present available to us, compounds containing large organic groupings, e.g. aromatic compounds and especially chelate compounds, have been found to be the most suitable. Such compounds can readily be prepared for most radioactive species, are frequently found to be readily volatile *in vacuo* at moderate crucible temperatures, and produce a deposit of which the mass and composition do not alter appreciably on exposure to the atmosphere.

Provided that reasonable temperature control is maintained during the distillation, charring of organic materials is not a problem. These compounds are generally of low mean atomic number with consequently low radiation-scattering characteristics, and also frequently exhibit optical absorption bands in the visible region. The latter are useful in the analytical applications to be discussed later.

As examples of the compounds used in specific cases, we may cite those on which we have already obtained preliminary results, namely nickel dimethylglyoxime for Ni^{63}, benzidine sulphate for S^{35}, and cobalt 1-nitroso-2-naphthol for Co^{60}, the $\bar{Z}$ values being respectively 4.19, 4.91, and 4.48. For the remainder of this paper, we will illustrate the techniques used mostly with data for nickel dimethylglyoxime, but much of the discussion is equally applicable in the case of other compounds also.

Nickel dimethylglyoxime is prepared (using microchemical techniques where necessary) according to the customary gravimetric analytical procedure, namely by the addition of alcoholic dimethylglyoxime and dilute ammonia to a warm slightly acid nickel solution. The precipitate is washed with warm

The authors are indebted to Mr. S. Fromson of Canadian Vickers Ltd. who prepared the wire from which the induction coil was made.

water, and then transferred to the distillation crucible as an aqueous or CCl_4 slurry. It is reslurried with CCl_4 and dried between distillations to re-establish thermal contact with the crucible. Distillation commences at a temperature of 120°C. under 1 μ Hg pressure.

The progress of the distillation can be followed for the first hundred micrograms of deposit by observation of the changing interference colors viewed from the reverse side of the film. These are quite brilliant even for compounds which are colorless by transmission. The distillation can be arrested at any time by admission to the apparatus of a small quantity of air via the leak referred to earlier.

In Fig. 6 are compared the optical absorption spectra obtained with a Beckman DU spectrophotometer from a colloidal solution of nickel dimethyl-

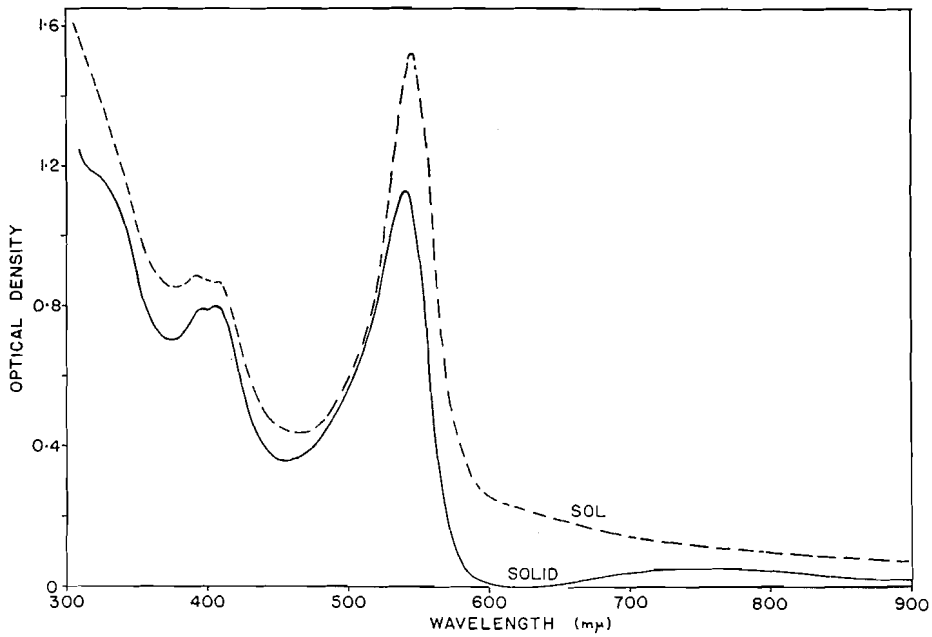

FIG. 6. Optical absorption spectrum of nickel dimethylglyoxime in the form of an aqueous colloidal solution protected by gelatin, and of the deposit after vacuum distillation.

glyoxime, and from the same compound as a deposit on VYNS film after distillation by the procedure outlined above. It is seen that the two are essentially identical (except for evidence of light scattering by the colloidal solution) indicating that the distillation process does not cause any significant decomposition.

Optical absorption on the 545 mμ peak is found in the deposit to be in accord with Lambert's Law for superficial densities up to about 150 μgm./cm.^{2}, and spectrophotometry may be employed to examine the thickness, evenness, and dimensions of the deposit. Fig. 7 shows a series of profiles or cross-sections of nickel dimethylglyoxime deposits of increasing superficial density, also

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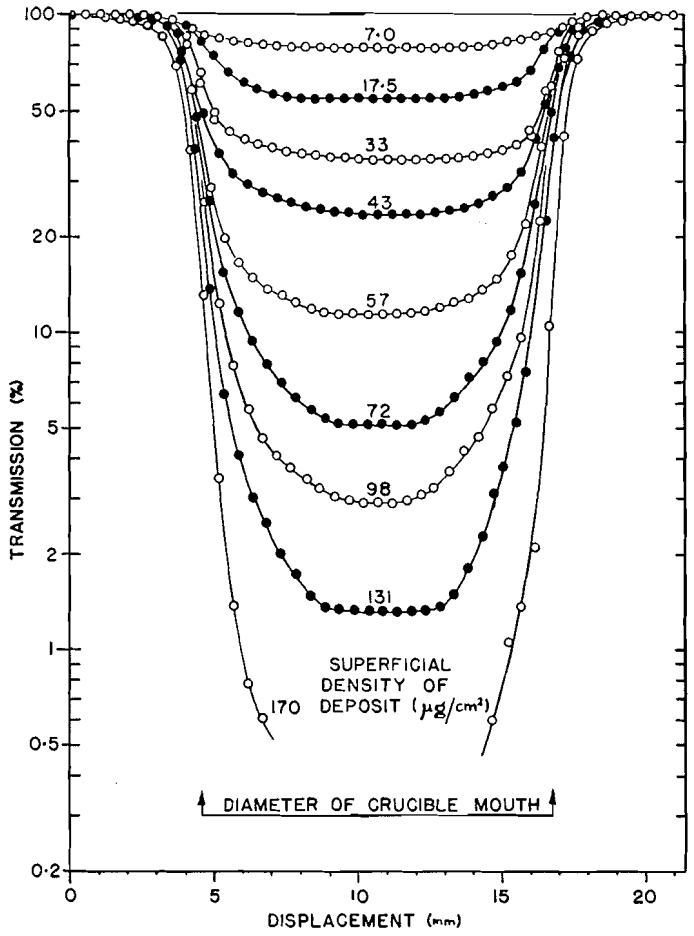

FIG. 7. Profiles of nickel dimethylglyoxime deposits of increasing superficial density, recorded with a slit width of 0.1 mm., and a wavelength of 545 mμ.

measured on a Beckman DU spectrophotometer. For these measurements the instrument was modified so that a micrometer screw and vernier scale controlled the movement of the film and deposit across the light path, and the slit was masked down to a length of 2 mm. at right angles to the direction of motion and a width of 0.1 mm. The transmission scale of this figure is logarithmic, so that vertical distances on this plot are proportional to deposit thickness.

It is seen that the diameter of the deposit does not alter sensibly with increasing superficial density, and profiles measured mutually at right angles show that the deposit is circularly symmetrical. Further, while the deposit departs considerably from the ideal of a right cylinder, the form of the profile is essentially constant with increasing thickness, and the mass of the deposit is nearly proportional to its effective superficial density for self-absorption purposes.

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The microstructure of the deposit is shown in Figs. 3 and 4. These are electron micrographs of cobalt 1-nitroso-2-naphthol and nickel dimethylglyoxime deposits of 1.2 and 5 μgm./cm.^{2} superficial density respectively.* These pictures are representative of several taken over different areas of deposit all showing a uniform distribution of crystals of about 1 μ in diameter. A single crystal layer is completed apparently at about 5 μgm./cm.^{2} and the same crystal size is maintained throughout the completion of several crystal layers.

(*b*) *Estimation of Self-absorption*

The method of self-absorption estimation used in conjunction with the proposed source preparation technique is essentially similar to the conventional technique used with end-window counters. That is, the apparent source specific activity is plotted as a function of source superficial density, and extrapolated to zero superficial density to obtain the true specific activity. The major difference is that when using a 4π-counter, instead of milligrams of source material, one has frequently a few micrograms, which must be measured with an accuracy of better than $\pm$ 0.5 to 1%.

It is probable that direct spectrophotometric measurements on the deposit as outlined above, or direct weighing with a balance of the necessary sensitivity, could be made into a satisfactory procedure for superficial density determina-

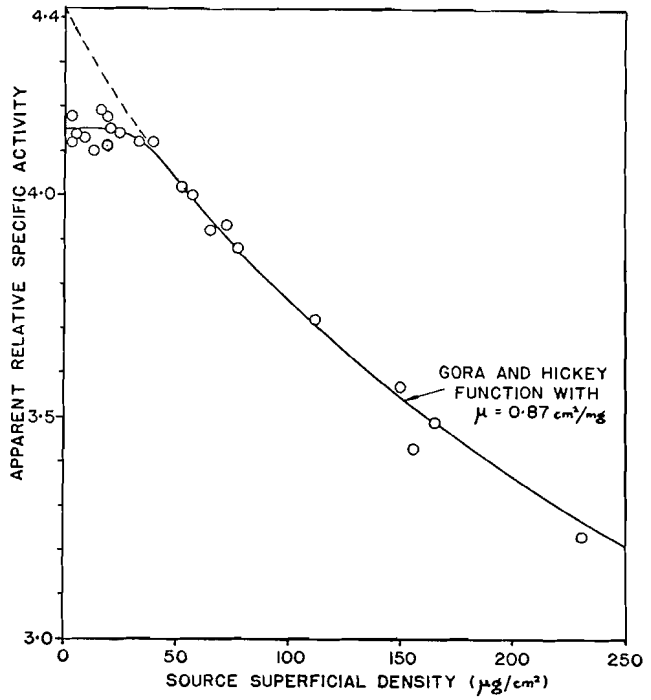

FIG. 8. Self-absorption curve for Ni^{63} beta-radiation in nickel dimethylglyoxime of 0–250 μgm./cm.^{2} superficial density.

The authors are indebted to Dr. A. W. Tickner of the Applied Chemistry Division, N.R.C., Ottawa, for use of electron microscope facilities.

tion. However in the case of nickel dimethylglyoxime we have found it more convenient to measure the apparent disintegration rate for each source prepared, and then to dissolve the deposit off the film with 1 N hydrochloric acid and determine the nickel colorimetrically by the procedure of Mitchell and Mellon (13), which can be made sensitive to 0.04 μgm. Ni. The efficiency of dissolution of the deposit from the film can be checked by drying the film again and making a second activity measurement in the counter. The activity found is generally a negligibly small fraction of the total originally deposited.

The results of such measurements on Ni^{63} beta-radiation and nickel dimethylglyoxime sources are shown in Fig. 8 for source superficial densities up to 250 μgm./cm^2.

C. DISCUSSION

Ni^{63} beta-radiation with an end-point energy of 67 kev. is the softest radiation studied in the present series of papers, and is with few exceptions as soft as any radiation liable to be encountered in 4π-counting work. It therefore forms a good test of any method for determining self-absorption losses, since absorption is at a maximum, the quantities of material handled are at a minimum, and any irregularities or irreproducibility of source material structure will produce a maximum scattering in the experimental data.

The data of Fig. 8 indicate that the proposed method of preparation produces sources in which self-absorption effects are satisfactorily reproducible. We have fitted to the data the self-absorption function given by Gora and Hickey (4) for a 2π-steradian geometry (which will be identical for a 4π-steradian geometry). This function was derived by integrating over a solid angle of 2π steradians the radiation intensity observed from a source of given thickness, making the usual assumption that absorption of beta-radiation is exponential with thickness. It is observed that the fit to our data is satisfactory above about 30 μgm./cm.^{2} and up to at least 250 μgm./cm.^{2} source superficial density. Our value of self-absorption coefficient, 0.87 cm.^{2}/mgm., is in reasonable agreement with the value predicted for a 67 kev. β-emitter by Baker and Katz (1), on the basis of self-absorption measurements on more energetic β-emitters in a rough approximation to a 4π-steradian counting geometry.

The anomalous absorption effects observed at superficial densities below 30 μgm./cm.^{2} we interpret as due to the finite crystal size of the source material. The method of plotting the data in Fig. 8 assumes that the method of source preparation results in a completely uniform distribution, whereas as is seen from Fig. 3 sources of very low apparent superficial density consist of well spaced crystals. Thus the true superficial density of the source material, i.e. of the crystals, is considerably greater than that measured. It is not until several crystal layers are built up that the measured superficial density approaches that of the source material proper, and regular self-absorption behavior is observed. Unlike the case with low-geometry counters, where self-scattering interferes (1, 2, 7, 14, 24), extrapolation of the curve obtained above 30 μgm./cm.^{2} to zero superficial density, as indicated by the broken line in Fig. 8, is expected to lead to the correct specific activity figure.

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We consider that the extrapolation as indicated or any other method of extrapolating the data presented will lead to a disintegration rate accurate to probably $\pm 1\%$. This accuracy will improve with increasing energy of radiation, both since absorption effects are smaller and since the regular behavior referred to above will commence at relatively lower superficial densities. This will result in experimental points nearer the specific activity axis and hence a more accurate extrapolation. Further publications dealing with extension of these methods to emitters of more energetic radiation will elucidate this point.

As in the case of film absorption discussed earlier (17), the availability of a series of self-absorption curves for sources of emitters of a range of radiation energies, mounted by the method suggested above (i.e. using materials of low and relatively constant $\bar{Z}$), would allow a self-absorption correction to be made for any source encountered in routine work. Such a set of curves could be checked as suggested by Smith (23), if the series of radiation emitters included several amenable to coincidence measurements. The extent of beta self-absorption could then be measured directly for each source thickness prepared.

However such a generalized means of correction is necessarily an approximation, owing for instance to changes in radiation energy spectrum from nuclide to nuclide. For the most accurate working a plot and extrapolation such as in Fig. 8 will need to be made.

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RECOMBINATION OF RECOIL FRAGMENTS IN NEUTRON-IRRADIATED POTASSIUM CHROMATE[1]

By A. G. Maddock and M. M. de Maine[2]

ABSTRACT

The kinetics of the process whereby the retention increases on heating previously neutron-irradiated potassium chromate have been investigated. The results cannot be explained by any unimolecular or bimolecular mechanism, nor by a combination of a few such steps. The data are not compatible with the commoner diffusion-controlled mechanisms. Experiments on solid solutions of potassium chromate in potassium fluoberyllate suggest that the process involves the recombination of the fragments from individual rupture events. A tentative hypothesis, analogous to the theory of the formation of very thin oxide films on metals, is advanced and it accounts for all the existing data.

INTRODUCTION

The salts of the oxy-anions, such as potassium chromate, are among the simplest compounds in which it is possible to study the chemical effects of radiative thermal neutron capture. Potassium permanganate was one of the first compounds in which these reactions, known collectively as the Szilard-Chalmers' Effect, were investigated (1). The nature of the fragments formed by the recoil following the dissipation of the excitation energy of the compound nucleus formed by thermal neutron capture, in one or more photons, has been studied (13). Libby proposed that the metal–oxygen bonds in those oxy-anions containing a normally electropositive central atom are broken heterolytically. Thus the recoil fragments formed in the permanganate include MnO_3^+, MnO_2^{+3}, MnO_3^{+5}, and possibly Mn^{+7} together with O^{-2} ions. The most convincing argument in favor of these fragments was based on the observation that upon solution of the irradiated permanganate in very alkaline solutions nearly all the activity was found as permanganate.

Since it is inconceivable that a species could be produced which could be oxidized to the heptavalent state by water, the observation suggests that the fragments all contain heptavalent manganese. An alternative explanation is, however, possible. The fragments may be able to undergo rapid exchange with permanganate ions in very alkaline solution. For example, this might be the case for a fragment containing pentavalent manganese, and giving MnO_4^{-3} in alkaline solution.

On Libby's hypothesis, the chromates should give CrO_3, CrO_2^{+2}, CrO^{+4}, and possibly Cr^{+6} ions. When the irradiated chromate crystals are dissolved in water prior to analysis, these fragments react with the water through hydration or reduction to give radioactive chromate and chromic ions respectively.

The first two of the fragments suggested by the hypothesis for the chromates are known to hydrolyze to chromate ions without reduction. But CrO^{+4}

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Contribution from The University Chemical Laboratories, Pembroke Street, Cambridge, England. This paper was presented at the Symposium on Nuclear Chemistry and Radiochemistry held at McGill University, Montreal, Que., September 7—9, 1955.
[2]*Lately Miss M. M. Moodie.*

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and Cr^{+6} may be reduced before hydrolysis can take place. The fraction of the radioactive chromium found as chromate after solution is called the retention. Further investigations (2, 6, 7, 10, 12, 14) have been unsuccessful in the rigorous confirmation of Libby's hypothesis, but on the other hand it is not contradicted by any of the experimental evidence.

The proportions of the different kinds of fragments appear to depend on the nature of the crystals used. For instance different retentions are found for anhydrous lithium, sodium, and potassium permanganates (14). There is also evidence that the retention in irradiated crystals depends on the mean recoil energy, and may therefore be different for different isotopes formed by a single neutron irradiation (9, 15).

Although the identities of the fragments are still in doubt, it has proved possible to study some of their reactions in the irradiated crystals. It is now clear that these studies constitute a new and valuable chemical approach to the investigation of lattice abnormalities and reactions in the solid state.

It was discovered by Williams (18) that the retention in antimony pentafluoride and ammonium fluoantimonate was increased when the neutron-irradiated crystals were subsequently irradiated with ionizing radiation. A similar effect has been observed with potassium chromate and a preliminary study of the kinetics of the process suggests a unimolecular process (10).

A similar thermal annealing process was discovered by one of the authors (11), and has since been shown to be quite general (4, 8, 10, 14, 15). A similar study of the kinetics of the process in potassium chromate crystals led to the conclusion that a very complex mechanism was involved (10). More recent work by Zuber (19), using cobaltic tris-ethylene diamine nitrate, was analyzed in terms of two unimolecular processes with energies of activation of 25 ± 5 kcal. and 20 ± 5 kcal.

The chemical nature of the thermal annealing process has been discussed by one of the authors (10). It might consist of a simple recombination of the original fragments, which are seldom separated by many lattice units. Alternatively, reactions may take place with nearby inactive chromate ions. Thus $*CrO^{+4} + CrO_4^{-2} \rightarrow *CrO_2^{+2} + CrO_3$ converts a reducible species, $*CrO^{+4}$, into an hydrating $*CrO_2^{+2}$ species; and a radioactive chromium atom previously destined to form a chromic ion upon solution will give rise to a chromate ion. Finally it is conceivable that purely electronic reactions are involved.

It seemed possible that one of these alternatives might be discarded if the behavior of irradiated homogeneous mixed crystals of potassium chromate and potassium fluoberyllate were examined.

A number of very careful measurements of the variation in the retention with the time of heating of crystals of pure potassium chromate and of mixed chromate – fluoberyllate mixed crystals have been made.

EXPERIMENTAL

A. Irradiation

The neutron irradiations were all carried out in a carbon stringer in the thermal column in the Harwell Graphite Pile shield. All samples for irradiation

were pumped on a high vacuum line for about an hour before they were sealed off, still under high vacuum, in quartz ampoules.

The combined neutron and radiation doses received by the samples are not accurately known, but an indication is given in the PFW factor. The nominal flux of the pile given by the Harwell Isotope Office in units of 10^{11} neutrons/cm.^{2}/sec. is multiplied by the number of weeks spent by the samples in the pile at that flux to give the radiation dose in units of PFW or pile-factor-weeks.

B. Materials

Analytical reagent quality potassium chromate was used without further purification.

Potassium fluoberyllate was made by dissolving a molecular weight of beryllium carbonate in 4.5 molecular weights of hydrogen fluoride (17). An aqueous solution of two molecular weights of potassium carbonate was slowly added. The water and excess hydrogen fluoride were evaporated by gentle heating and the fine crystalline potassium fluoberyllate product was recrystallized twice from water.

Mixed crystals of the isomorphous potassium chromate and potassium fluoberyllate were made by preparing an aqueous solution 97% saturated at 20°C. with potassium chromate, and then saturating this solution at the boiling point with potassium fluoberyllate. The mixed crystals of potassium chromate and potassium fluoberyllate were allowed to form slowly. They were then filtered and washed thoroughly with cold distilled water to remove all traces of adsorbed chromate. The crystals were dried *in vacuo*.

Optical examination of the product revealed a high degree of uniformity, and spectrophotometric measurements on aqueous solutions made from weighed portions of material indicated that the mixed crystals contained approximately 1 mole % of potassium chromate.

C. Analysis Method

Neutron-irradiated potassium chromate and mixed potassium chromate – potassium fluoberyllate crystals were analyzed by the method devised by Green, Harbottle, and Maddock (10). The irradiated solid was dissolved in an acid solution containing chromic and chromate carriers. In one aliquot, lead chromate was precipitated and dissolved to provide a solution which gave a measure of radioactive chromate. Sodium hydroxide – peroxide treatment oxidized chromic ions to chromate, and measurements on the solution of the lead chromate precipitate gave a measure of the total chromium activity.

D. Measurement of Radioactivity

The 325 kilovolt gamma-ray of Cr^{51} was counted by the use of a sodium iodide – thallium activated scintillation crystal and an adjacent photomultiplier tube to record the gamma-ray scintillations (3). The pulses from the tube were amplified and fed into a dual-discriminator anticoincidence pulse-height analyzer (5). Aliquots of the solutions were counted in an annular polythene vessel which surrounded the cylindrical crystal.

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RESULTS

The results are given as values of the retention. In previous work an insufficient number of values were obtained to permit a detailed study of the kinetics of the recombination reactions.

For potassium chromate irradiated for one week at a pile factor of 0.1, an average retention value of 69.1% was obtained. No change in this value was detected in material kept in air at room temperature for periods up to four months.

In Fig. 1 are given plots of the average retention values versus heating time at temperatures where a full range of determinations were made. During the first four hours, heat increases the retention quite rapidly to a value

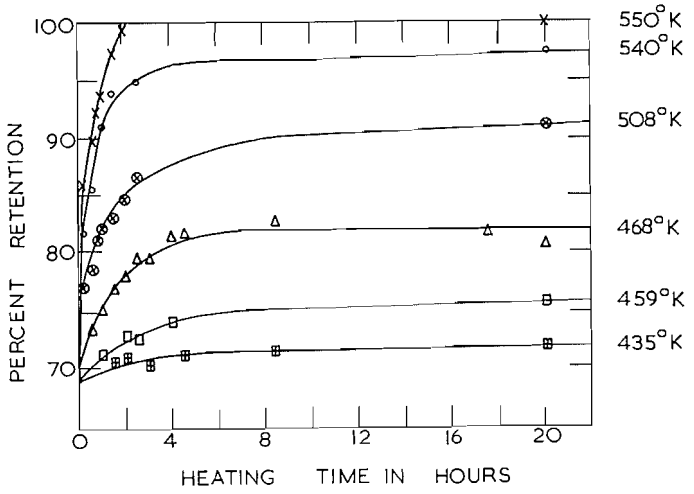

FIG. 1. Retention values versus time of heating at the temperatures indicated for potassium chromate irradiated for one week at pile factor of 0.1.

characteristic of each temperature. At times approaching a week, the effect has slowed to about a one per cent change per day. Fig. 2 shows that heat treatment at two different temperatures produces additive effects and that the retention value at which the rapid retention change ceases depends on the temperature of heating. Identically irradiated samples were heated *in vacuo* and in air. No differences in retention values were noted.

Potassium chromate – fluoberyllate mixed crystals irradiated for one week at pile factor 0.1 showed a 25.8% retention. Subsequent heating at temperatures similar to those used for the potassium chromate effected retention increases up to approximately eighty-five per cent. The heating curves for pure chromate and for the mixed crystals had a similar form, except that in the latter case the rate of retention increase "leveled-off" in approximately a quarter of the time.

DISCUSSION

Two questions are posed by these observations: the identity of the reacting species and the kinetic description of the process. The data does not provide

a real answer to the first of these questions; but the observation that the retention increases upon heating in a similar way in both irradiated potassium chromate and in irradiated dilute solid solutions of potassium chromate in potassium fluoberyllate suggests that the process does not involve the reaction of the "active" fragments with adjacent chromate ions but that it is due to recombination of the fragments following neutron capture. A reaction between a fragment destined to form a chromic ion upon solution (e.g. CrO^{+4}) and a fluoberyllate anion could conceivably produce a species which hydrolyzes to a chromate ion; but this appears to be a less likely explanation.

If it is supposed that the fragments formed by neutron irradiation are those suggested by Libby's hypothesis (13), and if it is assumed that Cr^{+6} ions could barely avoid electron capture for very long in the potassium chromate lattice, the reaction must be $CrO^{+4} + O^{-2} \rightarrow CrO_2^{+2}$.

Inspection of Fig. 1 shows that the process does not proceed by a simple unimolecular process, corresponding to the recombination of the fragments from individual eruptions, or by a bimolecular process such as would be found if the fragments from different primary events were as close to each other on an average as those from the same event. At each temperature the retention increases at first rapidly, and then more slowly until it reaches a nearly steady value after about six hours. With prolonged heating of the irradiated material, it can be shown that the retention continues to increase very slowly until it reaches 100%.

Zuber (19) has interpreted similar results in terms of two unimolecular processes. Two combinations of unimolecular processes are possible. If a single type of chromium fragment were liable to two processes leading to an increase in the retention, each characterized by a different activation energy, the kinetic behavior at any one temperature would be indistinguishable from that of a single unimolecular process. If, however, there were two kinds of chromium fragment, perhaps differing only in lattice situation, each with its characteristic activation energy for the process leading to an increase in the retention, then a plot of the logarithm of the proportion of unaffected fragments versus the time of heating should be capable of analysis into two linear portions. With this model, the second linear portion of the curves at different temperatures should extrapolate through a single point on the axis of the ordinate. This point would correspond to the proportion of the type of fragment responsible for the slower process and originally present in the irradiated crystals. These suppositions are obviously not true for the curves shown in Fig. 3.

These results cannot be interpreted in terms of even a small number of unimolecular processes. They are not compatible with a small number of bimolecular processes.

It might, however, be possible to interpret these results in terms of competing reactions. For instance, it is possible that the labile chromium fragments are liable to two reactions, one converting them to a chromate-forming species and the other to a chromic-forming species. A much slower reaction may be capable of converting the product of the second of these reactions into the

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product of the first reaction or into some similar body. If this model were correct, increasing the temperature after six hours heating, when the pseudo-equilibrium retention is reached, should have little effect on the retention except for the very slow process. In fact, Fig. 2 shows that the retention

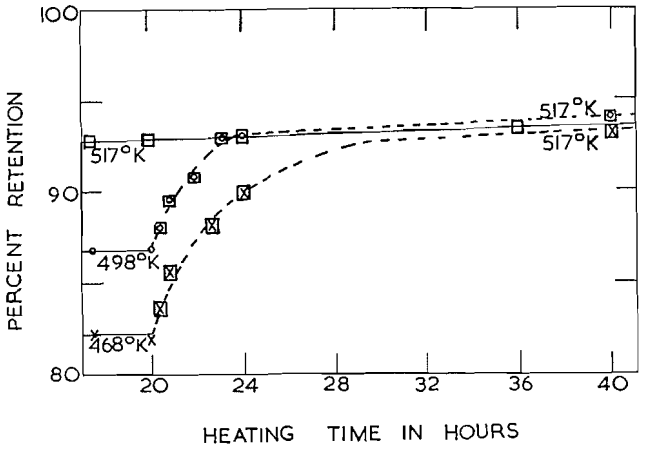

FIG. 2. For potassium chromate irradiated for one week at pile factor of 0.1; plots showing retention values in per cent versus heating time for material heated first at 468 °K. or 498 °K. and then at 517 °K. compared to the values for material heated only at 517 °K.

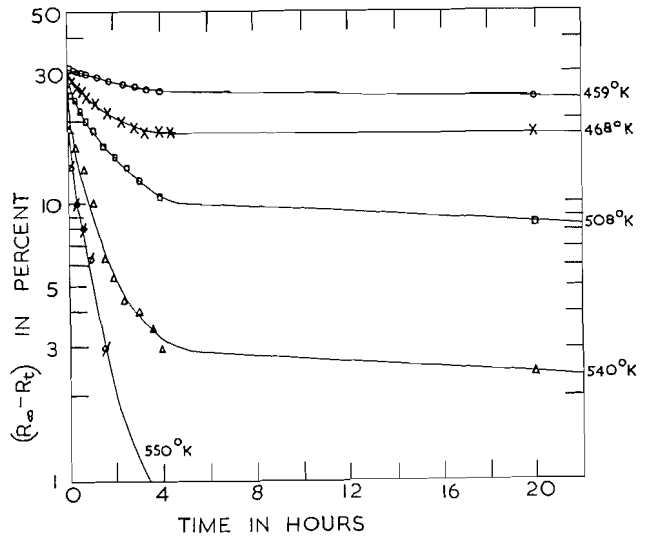

FIG. 3. For potassium chromate irradiated for one week at pile factor of 0.1; plots of the difference between the limiting retention value (R_∞) and the retention at time t (R_t) on a logarithmic scale, versus the time of heating.

quickly rises to the pseudo-equilibrium value appropriate to the new temperature. The progress of this change is similar to that in the initial process. This behavior is not compatible with the explanations already proposed in connection with Fig. 1, which are based on the assumptions of competing

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reactions. Retention changes are irreversible and are always in the direction of increasing retention. Subsequent cooling thus does not lead to reduction.

The nature of the process is indicative of a diffusion-controlled mechanism. Under certain circumstances this may lead to a parabolic or third order dependence on the time. Fig. 4, however, shows that no such power relation

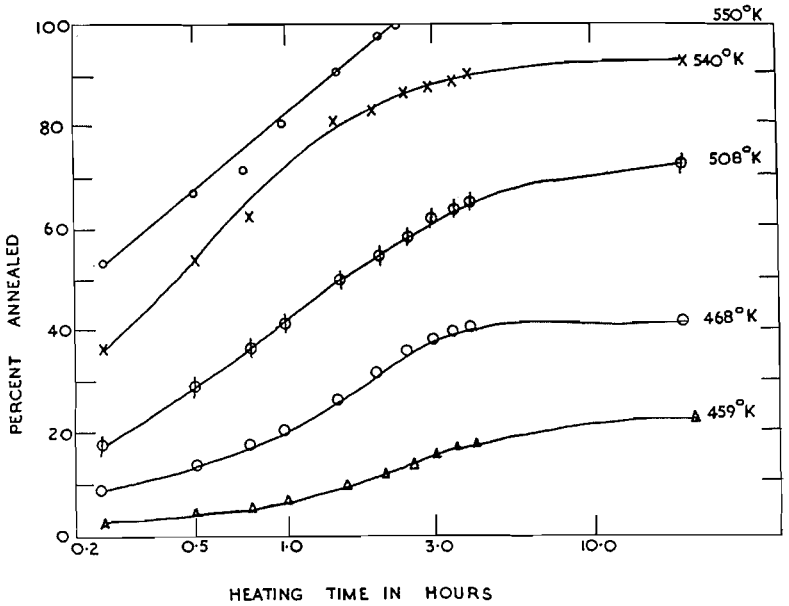
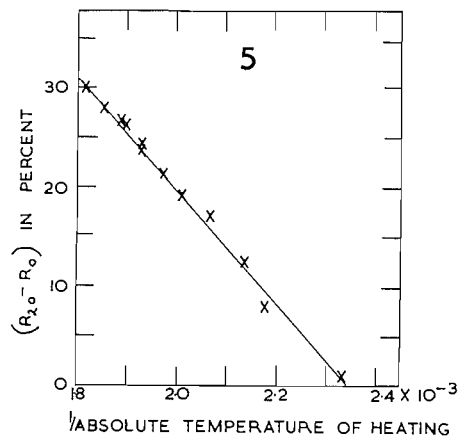


FIG. 4. For potassium chromate irradiated for one week at pile factor 0.1; plot of the percentage of the maximum retention change which has been effected versus the heating time in hours, on a logarithmic scale, for the heating temperatures indicated on the right of the figure.



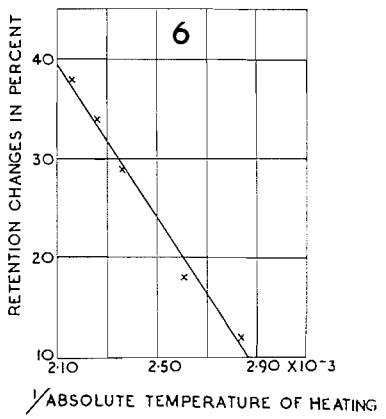


FIG. 5. For potassium chromate irradiated at pile factor 0.1; plot of the retention change effected by 20 hr. of heating versus the reciprocal of the absolute temperature of heating.

FIG. 6. For potassium bromate (8); plot of the retention change effected by the stage of heating during which the retention increase was rapid, versus the reciprocal of the absolute temperature of heating.

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between the extent of the reaction and the time of heating exists. Other relations have been derived for a mechanism involving a small number of diffusion jumps, but none of these predicts the pseudo-equilibrium after a few hours heating at each temperature which appears to be so characteristic of the process.

It is noteworthy that a simple linear relation is found between the change in retention from the zero-time value to the pseudo-equilibrium value and the reciprocal of the absolute temperature of heating. Fig. 5 shows the results obtained in this investigation and Fig. 6 shows the only other data in the literature that is sufficiently extensive for this type of treatment (studies made on irradiated potassium bromate (8)).

With regard to the identification of the reaction responsible for these effects which have just been discussed, it is interesting to inquire as to the type of kinetic behavior which would be predicted for such a process. The hypothesis postulates that a single reaction is involved: the recombination of active CrO^{+4} fragments with the oxygen ions that they lost upon formation. As the fragments do not recombine at an appreciable rate at room temperature, it must be supposed that the process has an activation energy, U. The CrO^{+4} and oxygen ion fragments will be supposed to be separated by various distances, X. With their opposite charges they will be electrostatically attracted and thus the effective energy of activation for the recombination process will be reduced.

The process now becomes analogous to the growth of the very thin oxide films treated by Mott (16). The rate of recombination at time t after commencement of heating will be given by the product of two terms,

$$dR/dt = e^{-U/kT}\, e^{V/kTX},$$

where X is the smallest separation of the fragments at time t, T is the absolute temperature, k is Boltzmann's constant, and V will involve the charge on fragments, dielectric constant, and other terms. Now a relation between R and X appears to exist.

Suppose that all the chromium fragments are placed at some common origin and their oxygen ion partners will be strung out in a line drawn from this origin. None will be closer than some separation of X_0 as all at smaller distances will be assumed to recombine immediately after formation to give rise to the zero-time retention of R_0. None will be farther away than some value X_∞ since the initial recoil can effect such a maximum separation. As R changes from R_0 to 100% by heating, the oxygen ions with separations ranging from X_0 to X_∞ will recombine with their partners. If the oxygen ions are uniformly distributed between X_0 and X_∞, the change in retention will be a linear function of X.

$dR/dt = e^{-U/kT}\, e^{V/kT(\Delta R + S)}$, where ΔR is the retention and S is some constant term.

This expression cannot be integrated simply but it does fit the data reported above and it explains all the salient features of this data. The kinetic aspects

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of the increase in retention on heating are therefore analogous to the formation of the very thin oxide films. When heating is begun, ΔR is small and the second term in the expression for dR/dt is large and dominates the rate of reaction. As ΔR increases the second term soon becomes approximately unity and the rate of retention increase is then determined by the first term which will be small if U is large. This corresponds to the ultimate very slow increase in retention.

Suppose we consider that the second term becomes effectively unity when $V/kT(\Delta R_e + S) = \alpha$. This expression will then relate ΔR_e, the pseudo-equilibrium change in retention to the temperature of heating, T. It also accounts for the experimentally observed linear relation between $1/T$ and ΔR_e.

A more detailed development of this model for the thermal recombination process and its relation to the kinetics of some of the processes in solids will appear in a subsequent publication.

ACKNOWLEDGMENT

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THE SOLVENT EXTRACTION OF PROTACTINIUM[1]

By A. Goble, J. Golden, and A. G. Maddock

ABSTRACT

The variation of the experimental extraction coefficient for protactinium upon dilution of the solvent ketone with benzene has been determined for aqueous solutions at constant concentration of hydrochloric acid. The bromo complex has been shown to be far less readily extracted. The effects on the extraction of the nitrate complex by amyl acetate, of the nitric acid, of the nitrate and hydrogen ion concentrations in the aqueous phase, as well as of the dilution of the solvent with benzene, have been explored. The existence of a slow reaction in the extraction has been demonstrated. It is concluded that chloride solutions are the more reliable for the isolation of protactinium from concentrates.

Several observations on the extraction of the complex chlorides and nitrates of protactinium from aqueous solutions by organic solvents have been reported. The earliest of these to become generally available were two very brief documents declassified by the United States Atomic Energy Commission in 1948 (6, 7). No details were included in these notes. However, a few quantitative observations on the extraction of protactinium, by 2,2′-dichlordiethyl ether, from aqueous solutions containing various concentrations of chlorides and hydrochloric acid, and for eight other solvents under fixed conditions in the aqueous phase, appeared in the following year (5).

Until quite recently the only additional information to appear was the description of the extraction by tributyl phosphate, diisopropyl carbinol, and diisopropyl ketone contained in a brief report on the separation of natural protactinium due to Elson *et al.* (1). A great deal more information became available with the publication of Volume 14A of Division IV of the National Nuclear Energy Series. Few of the original papers quoted in this volume (8–19) are available in England. Many of the investigations refer to extraction from solutions at moderate or high salt concentrations. Some early work by Yaffe *et al.* (19) on the extraction by ketones, and by a number of later workers on tributyl phosphate (17, 8), are mentioned. Various investigators have made use of solvent extraction in the separation of natural protactinium from refinery residues (14, 18). Cyclic procedures for this purpose have been made possible by Kraus and Garen's discovery that the extraction could be suppressed by fluoride ion, but again became possible when the free fluoride was complexed by aluminum ions (11). The most extensive studies reported, however, refer to the extraction by diisopropyl ketone from nitrate solutions (9, 10). Hyde and Wolf have shown that extraction by diisopropyl ketone is possible from simple solutions in nitric acid. They have studied the variation of the percentage extraction with the concentration of acid and also with the concentration of additional nitrate ions at constant acidity. Kraus and Van Winkle (13) are reported to have extended these studies to chloride systems and a few of their results are tabulated in Volume 14A. Diisopropyl

[1]*Manuscript received December 12, 1955.*
Contribution from the University Chemical Laboratory, Pembroke Street, Cambridge, England. This paper was presented at the Symposium on Nuclear Chemistry and Radiochemistry held at McGill University, Montreal, Que., September 7–9, 1955.

carbinol is alleged to be preferable in some respects to the ketone but no quantitative information has been published (16, 15). Mention is also made of the extraction of protactinium by amyl acetate (Volume 14A, p. 126) but the reference quoted appears to be erroneous. Two years ago, before the above information became available, a detailed study of the solvent extraction of protactinium was commenced in connection with a program for the separation of a quantity of natural protactinium. The results are more extensive than and, in some respects, different from those reported in Volume 14A of the National Nuclear Energy Series. Part of the results referring to chloride solutions will appear elsewhere (3). In this paper some additional data on chloride solutions will be presented together with some observations on nitrate solutions.

Kraus and Van Winkle (13) have concluded that chloride solutions are preferable for work with natural protactinium and that their behavior is generally more reproducible than that of nitrate solutions. A number of experiments in the exploratory stages of this investigation led to the same conclusion but some quantitative investigation of the nitrate system seemed desirable.

EXPERIMENTAL

Materials

The benzene and amyl acetate were analytical reagent quality solvents and were not redistilled before use. The diisobutyl ketone was a technical quality material but was purified by fractional distillation. The fraction used boiled between 166° and 168°. The commercial manufacture of diisopropyl ketone ceased during this investigation and the material used was prepared by the careful oxidation of 2,4-dimethylpentane-3-ol with cold potassium dichromate. The product was purified by fractional distillation and the fraction boiling between 124° and 126° was used.

All the experiments were conducted with natural protactinium. The separation of the stock material will be described elsewhere (2). The final purification was conducted with solvent extraction cycles using diisopropyl ketone and chloride solutions (3). The product was stored in solution in 6 *N* hydrochloric acid in a polythene vessel. The stock solution contained about 1 mgm./ml. of protactinium. Spectroscopic analysis showed that less than 2% of impurities was present (2).

Procedure

The solutions of the solvents in benzene were made up by volume. In all cases one milliliter volumes of solvent and aqueous phases were used. The aqueous phases were prepared by the addition of a standard aliquot of the protactinium stock to a much larger volume of solution made up to contain the desired concentration of acid and, in some cases, salts. The acidity of the resultant solution was redetermined by titration of an aliquot.

Losses of material by adsorption, or possibly ion exchange, on the walls of the containers were greatly reduced by the almost exclusive use of polythene vessels. These and other precautions are described elsewhere (3). Equilibration was achieved by the agitation of the snap-closure polythene capsules, used to

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contain the mixture, in a vigorous mechanical shaker for 10 min. No attempt was made to thermostat the mixture, since previous work on the chloro complexes only showed an extremely small temperature coefficient (3). Room temperature varied between 18° and 22°.

The protactinium was estimated by the measurement of its alpha activity in the two phases. Suitable aliquots from each phase were evaporated onto copper or aluminum foils and counted under a scintillation counter with standard geometrical conditions. Care was taken to check the activity balance and losses were kept below 1%.

Results

The effect of dilution of the solvent with benzene was investigated in 6 and 8 *N* hydrochloric acid solutions with diisopropyl ketone and at the latter acidity with diisobutyl ketone. The diisopropyl ketone solutions were pre-equilibrated with the 8 *N* hydrochloric acid before use. The results are shown in Fig. 1.

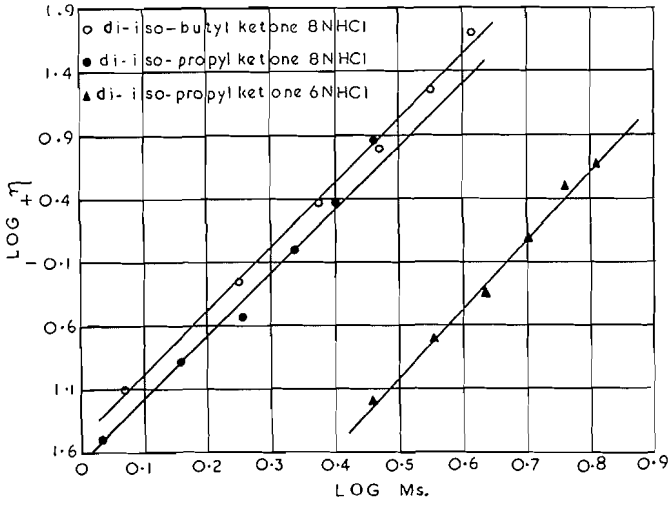

FIG. 1. Variation of η, the apparent extraction coefficient or ratio of protactinium in the organic and aqueous phases, with the molarity of the ketone in the benzene solution extractant.

A comparison of the behavior of the chloro and bromo complexes was made using diisopropyl ketone as solvent. The hydrobromic acid stock used was prepared by re-extracting a ketonic solution of the chloro complex with dilute hydrobromic acid and adjusting to 6 *N* in hydrobromic acid after separation. The original extraction was made from a sufficiently dilute acid solution to avoid any appreciable extraction of hydrochloric acid by the solvent. The results are shown in Fig. 2. The solvent was not pre-equilibrated with the various concentrations of acid used.

The extraction of protactinium from nitric acid or nitrate solutions by amyl acetate was found to increase with the time allowed for equilibration. Measurements were made at the end of the usual 10 min. agitation and also following a similar agitation after varying periods of time in quiescent contact. The

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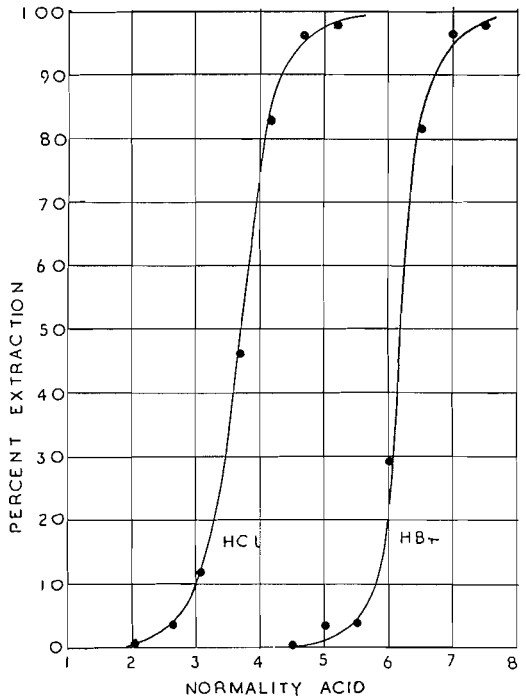

FIG. 2. Variation of the percentage extraction with the normality of hydrochloric or hydrobromic acids in the aqueous phase. Solvent: diisopropyl ketone.

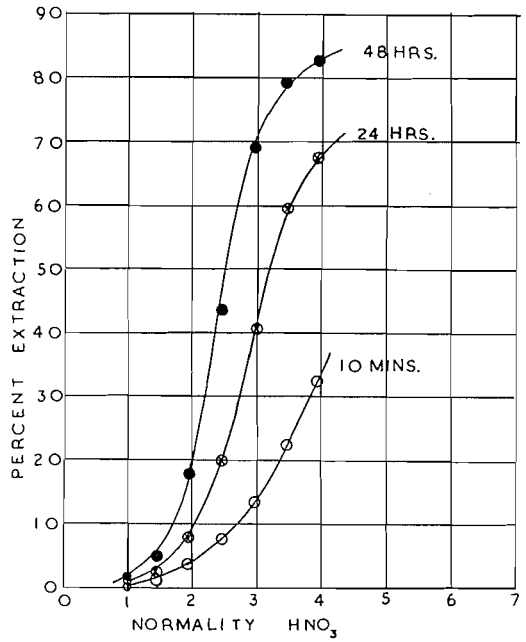

FIG. 3. Effect of time and concentration of nitric acid in the aqueous phase on the percentage extraction by amyl acetate.

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nitric acid stock was prepared in a similar manner to the hydrobromic acid solution. The results are shown in Figs. 3 and 4. In each case the solvent was pre-equilibrated with the appropriate concentration of acid before admixture with the active solution. The effect of the dilution of the amyl acetate with benzene was also studied after varying periods of equilibration. The results are shown in Fig. 5.

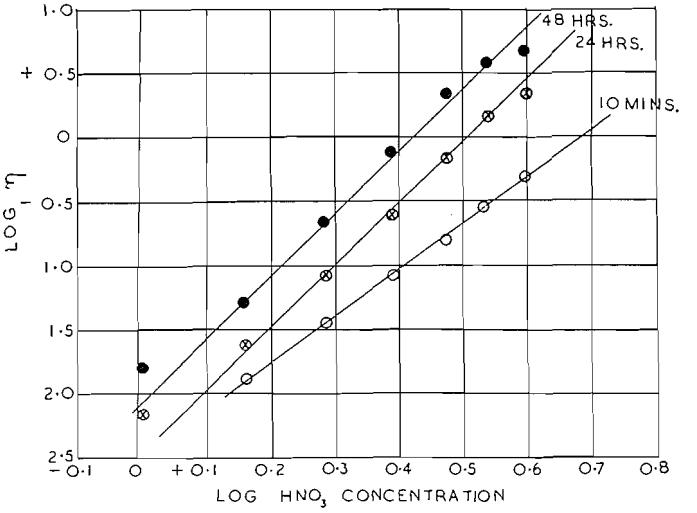

FIG. 4. Relation between η, the apparent extraction coefficient, and the concentration of nitric acid in the aqueous phase at various times. Solvent: amyl acetate.

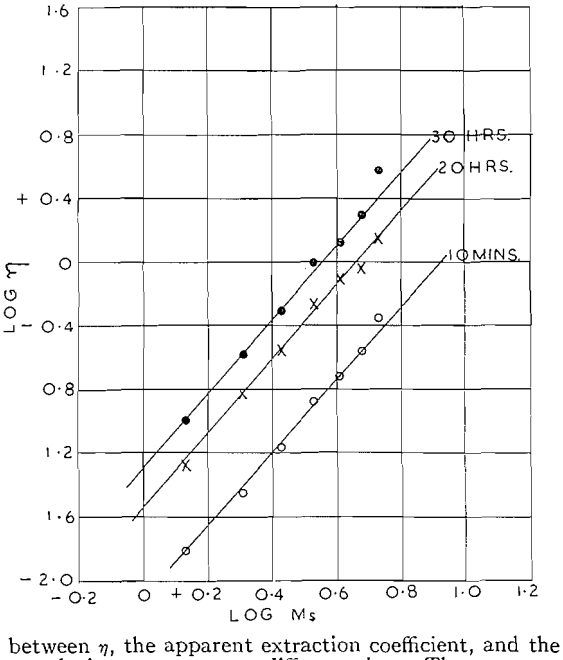

FIG. 5. Relation between η, the apparent extraction coefficient, and the molarity of amyl acetate in the benzene solution extractant at different times. The aqueous phase was in each case 5.75 *N* nitric acid.

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The effect of change in the acidity of the aqueous phase was studied at constant total nitrate concentration and approximately constant ionic strength by using various mixtures of nitric acid and ammonium nitrate. Measurements were made after various times of contact. The solvent was not pre-equilibrated with the aqueous phase before addition of the active solutions. The results are shown in Fig. 6. .

Finally the effect of increasing the nitrate concentration at constant acidity was studied. The influence of the time of equilibration was explored. The results are shown in Fig. 7.

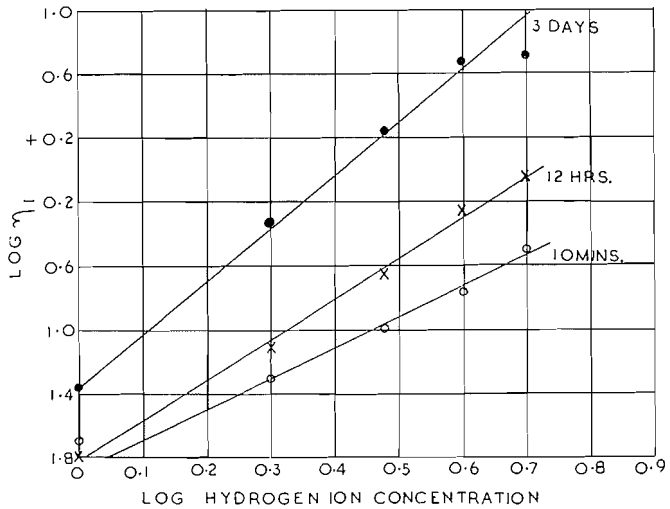

FIG. 6. Relation between η, the apparent extraction coefficient, and the concentration of hydrogen ions at constant nitrate concentration in the aqueous phase. Solvent: amyl acetate. All aqueous phases 6 M in nitrate.

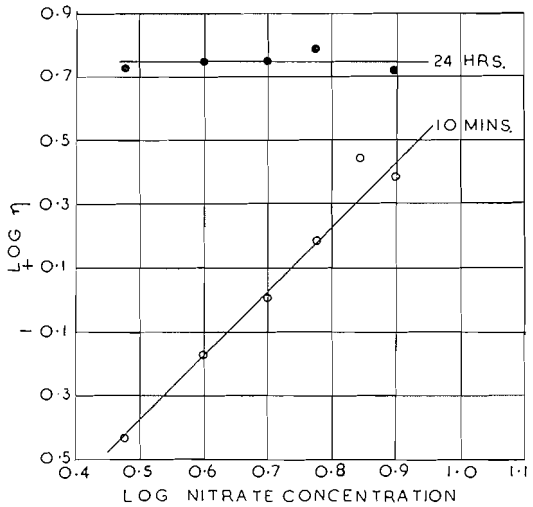

FIG. 7. Relation between η, the apparent extraction coefficient, and the concentration of nitrate at constant hydrogen ion concentration in the aqueous phase. Solvent: amyl acetate. All aqueous phases 3 N in acid.

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DISCUSSION

Most of the data reported above were obtained during a study of the separation of natural protactinium. They refer, therefore, to systems of empirical interest rather than to those that might be most illuminating from the point of view of the nature of the solvent extraction process. Thus the effect of only one of the relevant variables has been studied at constant ionic strength of the aqueous phase. A more detailed study, suitable for analysis in the manner developed by Irving and his collaborators (4), will appear shortly.

The apparent extraction coefficients, or ratios of protactinium in the organic to the aqueous phases, are considerably greater for strongly acid solutions and diisopropyl ketone as the solvent than any previously reported values (13). Indeed, they compare favorably with the values for highly salted solutions with other solvents. Except at the highest concentrations of acid neither ketone showed any considerable mutual miscibility with the aqueous phase. Neither did they extract hydrochloric acid in appreciable amounts.

The extraction of protactinium from hydrobromic acid only takes place at considerably higher concentrations than are necessary with hydrochloric acid. In neither case does the apparent extraction coefficient decrease again at concentrations of acid less than 8 *N*. Measurements have not been extended beyond this concentration because mutual miscibility becomes important. Unlike the majority of metals it appears that the bromo complexes are less stable than the chloro complexes of protactinium. A logarithmic plot of the apparent extraction coefficient against the concentration of acid in the aqueous phase is surprisingly nearly linear for both acids. The slope of these curves is about 14 for the hydrochloric acid and nearly 26 for the hydrobromic acid. These high slopes are due to the high activity coefficients of the acids in this concentration region, thus the slope of a similar plot using the activity of the acid is only 5 for the hydrochloric and about 9 for the hydrobromic acid. Such a result is compatible with, for instance, $PaOCl_6^{3-}$ and H_2PaCl_7 as the principal protactinium containing species in the aqueous and solvent phases, respectively, ignoring solvation.

The slopes of the plots shown in Fig. 1 are 5.2 and 4.9 for 6 and 8 *N* hydrochloric acid for the benzene dilutions of diisopropyl ketone, and 5.0 for 8 *N* hydrochloric acid and the benzene dilutions of diisobutyl ketone. Although these observations do not extend to such dilute solutions as would be desirable they indicate that the complexes extracted by either ketone are solvated with 5 molecules of that ketone. It will be noted that this figure is different from the value, 3, previously reported for diisopropyl ketone (3). The difference has been shown to be due to the presence of a small quantity of diisopropyl carbinol in the earlier samples of the ketone. The behavior of such mixtures will be discussed in a subsequent publication.

In the amyl acetate – nitric acid system the apparent extraction coefficient increases with time, Fig. 3, and the nature of the extracting complex changes. As a result the dependence of the apparent extraction coefficient on the hydrogen and nitrate ion concentrations in the aqueous phase changes with

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the time of equilibration. A nearly linear relation is found between the logarithm of the apparent extraction coefficient and the concentration of acid in the aqueous phase, in the absence of added salts, Fig. 4. The slope of the line, however, changes with the time of equilibration. The extraction by varying dilutions of amyl acetate in benzene, Fig. 5, suggests that the number of amyl acetate molecules associated with the complexes does not change. The slope of each line is about 2.3. A similar logarithmic plot shows that the apparent extraction coefficient depends on the 1.9 power of the hydrogen ion concentration after 10 min., the 2.6 power after 12 hr., and the 3.3 power after three days, all experiments being conducted at constant protactinium and nitrate concentrations, Fig. 6. The nitrate dependence, at constant acidity, however falls from the second power at 10 min. to independence at 24 hr.

It is not difficult to suggest species satisfying the behavior of the protactinium after long periods of equilibration, for instance, the third power dependence on hydrogen ion concentration and independence of nitrate concentration would arise if the complex were $HPaO(NO_3)_4$ and the dominant species in the aqueous solution $PaO_2(NO_3)_4^{3-}$. It is more difficult to suggest plausible initial species since the dependence on the second power of both the hydrogen and nitrate ions requires that both complex and aqueous species are either charged or uncharged.

The possibility that this slow change is due to hydrolysis of the amyl acetate has been considered. No considerable decomposition of the ester takes place during the period of the experiments. Addition of acetic acid up to 5% has little influence on the extraction. Amyl alcohol does enhance the extraction but seems unlikely to be responsible for the above-mentioned changes.

Both the nitrate and bromide complexes appear to be weaker and less readily extracted than the chloride complexes. Solutions of the former complexes in both aqueous and organic solvents more readily lose protactinium on the walls of containers than do the chloride complexes. These disadvantages taken in conjunction with the evidence of slow changes in the nitrate systems clearly indicate that chloride solutions are most suitable for extraction purposes.

The work described in this paper was subsidized partly by the British Admiralty and partly by the United Kingdom Atomic Energy Research Establishment. One of the authors (J.G.) was attached to the Services Electronics Research Laboratory, Royal Naval Scientific Service, during the period of these studies, and another (A.G.) acknowledges a grant from the United Kingdom Atomic Energy Research Establishment.

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THE YIELDS OF ^{129}I IN NATURAL AND IN NEUTRON-INDUCED FISSION OF URANIUM[1]

By B. C. Purkayastha[2] and G. R. Martin

ABSTRACT

Measurements have been made, by a radioactivation technique, of the ^{129}I formed in uranium by pile-neutron-induced fission, and in pitchblende by the natural fission of uranium. The amount found in the pile-neutron-irradiated uranium corresponds to a fission yield of 0.90% at mass 129. The natural production of ^{129}I in pitchblende is discussed in the light of the mass-spectrometric measurements of spontaneous fission xenon made by Thode and his collaborators. An upper limit of 1 part in 10^8 can be set for the occurrence of ^{129}I in natural iodine. The pile neutron capture cross section of ^{129}I has been measured as 35 barns.

INTRODUCTION

The measurement of the yield of one of the products of the spontaneous fission of uranium may be approached in one of two ways: by measurement of the activity in secular equilibrium with a known quantity of uranium, or by measurement of the rate of accumulation of a stable end product. The first method, although simple in principle, involves an extremely difficult decontamination problem in all but the most favorable cases. The second approach demands a degree of freedom from contamination by 'primordial' material isotopic with the substance sought which is unlikely to be attainable except in the case of the rare gases Xe and Kr. There is, however, a small intermediate class of nuclides with half-lives so long that a substantial mass of product can be accumulated, but at the same time short enough to ensure the complete absence of 'primordial' contamination. There are few such bodies amongst the products of the fission of uranium, and of these only one, ^{129}I, lends itself to estimation (by radioactivation (6)) in the extremely small amounts likely to be encountered.

The procedure adopted involved:

(*a*) the extraction of iodine from the sample, after addition of a known amount of carrier, using a method such that the chemical yield could be assessed in terms of the measured yield of carrier material, and

(*b*) the estimation of the ^{129}I by neutron activation, measuring the 12.6 hr. ^{130}I produced.

The same procedure was used to estimate the yield of ^{129}I in the pile-neutron-induced fission of uranium. Incidental to the main measurements are values obtained for the pile neutron capture cross section of ^{129}I, and for an upper limit to the natural abundance of this nuclide.

EXTRACTION OF ^{129}I FROM PITCHBLENDE

A rough calculation showed that it would be necessary to use about one kilogram of pitchblende for each determination, and it was necessary to

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Contribution from the Londonderry Laboratory for Radiochemistry, University of Durham, Durham, England. This paper was presented at the Symposium on Nuclear Chemistry and Radiochemistry held at McGill University, Montreal, Que., September 7–9, 1955.
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extract from this a known (preferably high) proportion of its fission product iodine content without the addition of more than a few milligrams of carrier iodine.

Two means are available to ensure that the chemical yield of carrier shall be equal to that of the fission product iodine (which may, initially, be in any one of four valency states): (i) to recover virtually 100% of both; or (ii) to effect complete equilibration between carrier and trace material before any separation is made. In the method finally adopted, it was demonstrated that yields of better than 98% were obtained in a preliminary separation involving the distillation of elementary iodine from the pitchblende solution. Since, during this step, *all* the iodine was in the elementary form, equilibration must have been complete, and no fractionation of carrier from carried material could have occurred in the course of subsequent purification. This procedure was tested with small quantities of pile-irradiated pitchblende in which it may be assumed that the iodine resulting from neutron-induced fission is in the same form as that from spontaneous fission.

The method used was as follows:

(i) Two-hundred-gram lots of pitchblende were placed in a flask with about 0.1 mgm. carrier iodine in the form of potassium iodide and the mineral dissolved, under reflux, in nitric acid (the only reagent which satisfactorily attacked all our pitchblende samples). It is to be expected that during this process of dissolution iodide will be oxidized to elementary iodine, and some of this may well be further oxidized to iodate; in addition the spontaneous fission product iodine may, in part, have been present initially in this form.

(ii) Nitrous fumes were removed by a current of nitrogen and a further 0.1 mgm. of carrier iodine added. The solution was then distilled until 80% of the total volume had passed over. A curious feature of this process is the fact that, although the major part of the iodine comes over quite quickly, a substantial fraction distills only after about 60% of the original volume has come over. Table I shows a typical distribution of the activity from a sample

TABLE I

DISTILLATION OF IODINE FROM 1100 ML. OF SOLUTION OF PITCHBLENDE IN NITRIC ACID: DISTRIBUTION OF ACTIVITY IN DISTILLATE

ml. distilled	% of activity recovered
170	63
220	8
170	3.6
130	2
220	21
910 ml.	97.6%

of pitchblende treated in this way. Similar distributions of activity were obtained whether the active iodine was added as iodide, iodate, or in the form of neutron-irradiated pitchblende.

The carrier iodine was normally lightly labelled with 8 day ^{131}I to facilitate the estimation of chemical yields; this activity was in any event small, and was

allowed to decay away before the radioactivation measurements were made.

(iii) The iodine distilled from the pitchblende solution was trapped in caustic soda solution which was subsequently evaporated to small bulk, and a further distillation step (with nitric acid + oxalic acid) carried out. The distillate from this operation was trapped in carbon disulphide, from which the iodine was extracted by alkaline sulphite and reduced to a standard volume (10 ml.) for measurement by means of a liquid counter (by comparison with a further aliquot of the initial carrier solution).

(iv) Four or five such operations, using 200 gm. of pitchblende, were carried out and the products combined for the preparation of a source for radioactivation analysis.

EXTRACTION OF ^{129}I FROM PILE-IRRADIATED URANIUM METAL

The chemical problem here is a good deal simpler than in the mineral case, since one starts with a chemically pure material; one, furthermore, in which the iodine may be expected to be present in a reduced form (7). Three 5 gm. pieces of uranium metal which had been irradiated in the Harwell pile ('BEPO') and allowed to 'cool' for about one year were available. ^{129}I would be effectively the only remaining radioactive iodine isotope after such a period.

The uranium pellets were dissolved, under reflux, in 50% nitric acid containing 0.5 mgm. of ^{131}I-labelled iodine in the form of iodate. After dissolution, a further 0.5 mgm. of iodine was added (also as iodate) and the solution diluted fivefold. Oxalic acid was then added, and the iodine distilled from the solution and trapped in alkali as before. The subsequent purification of the iodine so collected was carried out in the manner already described for the pitchblende samples.

RADIOACTIVATION PROCEDURE

The relevant neutron-induced reactions are:

$^{129}I(n, \gamma)^{130}I$ (12.6 hr. β emitter)

$^{127}I(n, \gamma)^{128}I$ (25 min. β emitter)

$^{127}I(n, 2n)^{126}I$ (13 day β^+, β^- emitter).

Neutron irradiations were made in BEPO at a flux of $\sim 1.5 \times 10^{12}$ n./cm.^{2}/sec. for one day. Approximately 14 hr. elapsed between the end of the irradiation and the start of counting of the samples, largely accounted for by the time for transporting the irradiated material from Harwell to Durham. The 25 min. ^{128}I had by then decayed away to a negligible level, leaving only the 13 day ^{126}I to be resolved from the ^{130}I activity. The residual 13 day activity was in fact used to measure the chemical yield in the preparation of samples for activation analysis. In addition, small pieces of thin copper wire ($\sim$2 mgm. each) were simultaneously irradiated, to serve as a 'flux monitor'; the ^{64}Cu activity induced in the copper,

$$^{63}Cu(n, \gamma)^{64}Cu(12.8 \text{ hr. } \beta^-, \beta^+, K),$$

has a half-life value so close to that of the ^{130}I activity being measured that an accurate knowledge of the time-dependence of neutron flux is not needed.

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(*i*) *Preparation of Samples for Radioactivation Analysis*

Iodide carrier was added to the samples, sufficient to bring the total iodine content to about three milligrams, and the solution made slightly acid with hydrochloric acid. Palladous iodide was then precipitated by the addition of a 1% aqueous solution of palladous chloride (16). The precipitate was filtered off on a small asbestos pad held in a constriction in 5 mm. tubing, and washed with a small quantity of water. The filter tube was cut, and the portion containing the precipitate dried thoroughly at 110°C. before placing inside a silica tube which was then evacuated and sealed. The end of the silica tube containing the palladous iodide was then heated for one hour at 370°C., during which time the iodine which was quantitatively liberated was distilled into the other end of the tube which was subsequently sealed off at a constriction. The elementary iodine contained in the small silica ampoule so formed was sent for irradiation together with

(*a*) a weighed sample of isotopically normal lead iodide, and

(*b*) a weighed piece of thin copper wire,

each being contained in similar silica ampoules, all of which were placed within the same aluminum capsule for irradiation.

(*ii*) *Treatment of Iodine Samples after Irradiation*

The following sequence of operations was designed to isolate the iodine activity free from any possible contamination by bodies with similar half-lives (especially 15 hr. ^{24}Na, 12.4 hr. ^{42}K, and Br (4.5 hr. + 36 hr.)) which might present difficulties in resolution.

The silica tube containing the iodine was crushed under water containing about 40 mgm. of carrier iodine as iodide. About one milligram of iodine was also added as iodate, and the whole reduced to iodide. The solution was made alkaline and boiled to ensure complete equilibration of the carrier with any iodine adsorbed on the silica of the ampoule. Potassium bromide was added as holdback carrier, and the iodine distilled from the solution after addition of sodium nitrite and sulphuric acid.

The distillate was collected in alkaline sulphite with more added bromide holdback, and iodine extracted into carbon tetrachloride after addition of sodium nitrite and sulphuric acid. The iodine was recovered from the organic layer after separation, by shaking with fresh alkaline sulphite containing more potassium bromide. This cycle of oxidation, extraction, reduction, and de-extraction was repeated four times to ensure that the iodine finally counted was free from impurities, especially from active bromine nuclides—bromide ion is not oxidized by acid nitrite solution, and does not therefore extract.

Iodine was finally precipitated as cuprous iodide by the addition of sulphur dioxide and cupric sulphate solution. The precipitate centrifuges well and spreads uniformly on the counting planchettes. Counting was carried out in a reproducible position close to the mica window of a 'bell-jar' type of Geiger–Müller tube, and was continued long enough to obtain a decay curve from which could be resolved the ^{130}I and ^{126}I activities.

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(iii) Treatment of Lead Iodide and Copper Samples

The lead iodide ampoules were treated by essentially similar procedures to those outlined above although speed was no longer necessary, and the need for so rigorous a purification was less. Samples were finally mounted as cuprous iodide, and the 13 day ^{126}I activity measured.

The copper wire was dissolved in nitric acid containing a known weight of cupric ion as carrier. The solution was scavenged by precipitating from it small quantities of silver chloride and of ferric hydroxide, and the copper finally precipitated as cuprous thiocyanate. The precipitate was washed, slurried with acetone, and mounted on nickel planchettes for counting as above.

(iv) Treatment of Counting Results

Corrections were applied where appropriate

(*a*) for 'losses' due to the finite resolving power of the counting apparatus,

(*b*) for differences in self-absorption correction between sources (from an empirical correction curve),

(*c*) for radioactive decay,

(*d*) for chemical yield. (Chemical yields in the radioactivation procedure were estimated by comparison of the ^{126}I activities induced in the weighed lead iodide sample and in the unknown, respectively.)

Activities were finally expressed with reference to a hypothetical thinly-spread source containing the whole of the activity at an arbitrary zero-time.

(v) Calibration of Radioactivation Procedure

To render absolute the relative measurements made by the radioactivation procedure, an irradiation was carried out as described above, of a sample of palladous iodide prepared from iodine extracted from an old pile-irradiated uranium slug.*

Fission product iodine is largely ^{129}I (after the short-lived species have decayed away) and it is possible to calculate with fair precision the amount of this nuclide in the sample irradiated, and thus to obtain a value for the ratio

$$\frac{^{130}I \text{ activity/mgm.}^{129}I \text{ irradiated}}{^{64}Cu \text{ activity/mgm.Cu irradiated}}$$

needed for the absolute evaluation of the radioactivation measurements.

ESTIMATION OF NUMBER OF FISSIONS IN IRRADIATED URANIUM SAMPLES

In the absence of precise information as to the integrated neutron dose received by the irradiated uranium pieces, the total number of fissions which had occurred in each was estimated, after dissolution and extraction of the iodine, by an absolute measurement of the ^{144}Ce fission product β-activity in an aliquot of the resulting solution. A known quantity of cerium carrier was added and cerium precipitated as cerous fluoride. A succession of reprecipita-

*We are grateful to Dr. W. J. Arrol of the Atomic Energy Research Establishment, who carried out this extraction.

tions was then carried out (as fluoride, hydroxide, and iodate in turn) with holdback carriers for those elements represented by long-lived fission products, and an aliquot of the ultimate solution finally mounted for counting. A gravimetric determination of cerium in the remainder of the solution gave a value for the chemical yield of the purification procedure.

The β-particles from ^{144}Ce are rather soft, and the counting measurement was actually made on the much more penetrating β-particles from the ^{144}Pr daughter, the ^{144}Ce radiation having been filtered out from the equilibrium mixture. The efficiency of the counting apparatus was determined by means of the UX_2 β-radiation in equilibrium with a known mass of uranium.

RESULTS AND DISCUSSION

(*i*) *Capture Cross Section of ^{129}I for Pile Neutrons*

From the irradiation of the weighed sample of fission product iodine we obtain, after correction for chemical yield, radioactive decay, etc.:

$$\frac{^{130}\text{I activity/atom } ^{129}\text{I}}{^{64}\text{Cu activity/atom } ^{63}\text{Cu}} = 14.2$$

so $\sigma_{129} = \sigma_{63} \times 14.2$, since $\lambda_{130} \simeq \lambda_{64}$. Here σ_{129} is the pile neutron activation cross section for ^{129}I, and σ_{63} is the similar quantity for ^{63}Cu (relating only to that fraction of the product which decays by β emission). Recent values for the neutron capture cross section of copper are 3.4, 3.50, 3.66, 3.63, and 3.57 barns (1, 3, 10, 4, 11). Taking an average value of 3.5 barns, and using the ratio $\sigma_{63}/\sigma_{65} = 2.3$, obtained mass-spectrometrically by Reynolds (13), we obtain $\sigma_a^{63} = 4.24$ barns, in good agreement with the value 4.3 barns quoted by Pomerance (12). If allowance is made for the fact that 42% of the ^{64}Cu disintegrations go by K-electron capture (5), and will not be recorded in our measurement, the value of σ_{63} to be used is $4.24 \times 0.58 = 2.46$ barns (cf. 2.8 barns obtained by Seren *et al.* (15)).

Using this value, we obtain for the pile neutron capture cross section of ^{129}I the value of 35 barns.

(*ii*) *The Yield for Mass 129 in Pile-neutron-induced Fission*

From the ratio of ^{130}I activity induced in a known mass of ^{129}I to that induced in the samples of iodine extracted from neutron-irradiated uranium we deduce the yield of ^{129}I in pile-neutron-induced fission. Two independent measurements gave values 0.89% and 0.92%. It is known from the work of Thode and Graham (17) that the independent yield of ^{129}Xe in pile-neutron-induced fission is negligible, so that the value, 0.9%, represents the total yield for this mass.

(*iii*) *Upper Limit to Natural Abundance of ^{129}I*

From the absence of ^{130}I activity from the irradiated samples of natural iodine it is possible to set an upper limit to the natural abundance of ^{129}I. We conclude that the ^{129}I/^{127}I ratio in natural iodine is less than 10^{-8}. In view of the shortness of the half-life (8) of ^{129}I in relation to geological time, this result is not unexpected, but it does reduce by a factor of 30 the upper limit previously set by mass-spectrometric investigation (9).

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(iv) The ^{129}I Content of Pitchblende

Three samples of pitchblende were investigated, of which only two yielded a final result from which could be calculated a value for the mass of ^{129}I in secular equilibrium with the uranium in the pitchblende. Table II summarizes the

TABLE II

RESULTS OBTAINED FROM TWO SAMPLES OF PITCHBLENDE

	Sample A	Sample B
% U_3O_8 in mineral	82%	64%
^{129}I yield (relative to spontaneous fission rate)	0.48%	0.54%
^{129}Xe yield (relative to total fission rate)* (adjusted to give ^{136}Xe yield = 6.5%)	0.222%	0.301%
Neutron fission rate as fraction of spontaneous fission rate†	0.32	0.49
^{129}Xe yield (relative to spontaneous fission rate)	0.29%	0.45%

**Mass-spectrometric results kindly made available by Dr. W. H. Fleming.*

†Calculated from ^{129}Xe yields on assumption that the fission yield for mass 129 is 0.90% for neutron-induced fission, and 0.01% for spontaneous fission.

results obtained for the two samples. On the assumption that secular equilibrium has been achieved, the apparent fission yield has been calculated as the ratio

$$\frac{\text{disintegrations of } ^{129}\text{I per second}}{\text{spontaneous fissions per second}} \times 100$$

using the ^{129}I half-life obtained by Katcoff, Schaeffer, and Hastings (8) and Segrè's value (14) for the spontaneous fission disintegration constant of uranium.

Dr. W. H. Fleming has kindly carried out mass-spectrometric examinations of the xenon from these two samples of pitchblende, with results also shown in Table II. It is clear from the work of Fleming and Thode (2), and of Wetherill (18), that in a mineral such as pitchblende by no means all the fissions occurring are spontaneous. Furthermore, it is clear that the distribution of products in this mass region is not by any means the same for spontaneous fission and for neutron-induced fission, and that, in particular, the yield at mass 129 in spontaneous fission is very small indeed. The mass-spectrometric measurements give only relative branching ratios for the various stable xenons, and it is necessary to assume a fission yield for one isotope. The values quoted have been adjusted to give 6.5% for mass 136, to agree with the 'smoothed' value for this mass in the neutron fission of uranium; since the yield curve for spontaneous fission has somewhat sharper peaks than the corresponding curve for neutron fission, this estimate may be slightly low. Fission yields obtained in this way have a significance somewhat different from that quoted for ^{129}I; for the mass-spectrometric values, the fission yield is given by the ratio

$$\frac{\text{atoms of } ^{129}\text{Xe formed per second}}{\textit{total} \text{ fissions occurring per second}} \times 100$$

and in Table II we quote also values which we have obtained by adjusting Dr. Fleming's results to the basis on which the ^{129}I yields were calculated.

This has been done by using his measured ^{129}Xe yield to deduce the proportion of neutron-induced fissions in the two samples, and then multiplying his yields by the factor

$$\frac{\text{spontaneous fission rate} + \text{neutron fission rate}}{\text{spontaneous fission rate}}.$$

Bearing in mind the various potential sources of error in this comparison (and especially the fact that the assumed value of 6.5% for the yield of mass 136 in spontaneous fission may be too low) the discrepancy between the two results for sample B is not excessive. The agreement is poorer for sample A, and is in a sense (more ^{129}I than would be expected from the ^{129}Xe result) difficult to explain by any reasonable geochemical hypothesis; it represents an increased yield from neutron fission of uranium during recent geological time whereas the most plausible natural changes (especially radioactive decay of ^{235}U) would tend to produce the opposite effect.

ACKNOWLEDGMENTS

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CHEMICAL EFFECTS OF THE NUCLEAR TRANSFORMATION $N^{14}(n, p)C^{14}$ [1]

By Peter E. Yankwich

ABSTRACT

The physical and chemical behavior of energetic carbon particles in ionic lattices is investigated. Models of the process due to Libby and to Seitz and Koehler are compared for simple and complex ionic crystals. For simple crystals the models lead to practically identical chemical predictions; where polyatomic ions are present, the Seitz–Koehler model appears to give a more satisfactory account of the distribution of radiocarbon over various product species.

INTRODUCTION

There has been considerable experimental effort directed at the elucidation of the chemical consequences of radiative neutron capture reactions; there, the target and product atoms are similar chemically, the recoil energy of the product is modest, a few hundred electron volts at most, and re-formation of the parent molecules may occur. In the case of typical (n, p) reactions, the product recoil energies are of the order of tens of thousands of times chemical bond energies, the product fragment is a chemical impurity in the target substance, and the atomic number change makes it difficult to think of "retention" of the product atom. There has been comparatively little experimental or theoretical work published on (n, p) reactions. It is the purpose of this paper to attempt a correlation of the results of recent research in this area. As a matter of convenience, the discussion will be related to ionic crystals; the extension to molecular and valence solids can be made with little difficulty.

PHYSICAL PROCESSES

*Early History of a Carbon Hot-atom**

At the moment of its creation, the C^{14} particle is in the state of a quadruply charged negative ion with a kinetic energy of about 40 kev. The velocity of this particle is that of an electron of 1.56 ev. energy; therefore all electrons bound to it by less than that energy will be swept off by the field of the ions in the lattice (18), and it will be ineffective in causing the excitation of any electron unless the energy required for such a transition is close to 1.56 ev. (14). The electron affinity of the neutral C atom is about 1.2 volts (12), so a swiftly moving C^{14} archekine may exist as a C^- ion when its kinetic energy has been

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**The problem of terminology in the field of "hot-atom chemistry" has been reviewed by Willard (27). In systems such as those which are the subject of this paper, one could apply terms such as: activated, energetic, hot, recoiling, to the C^{14} product particle with equal correctness. Each of these terms, however, is applicable not only to the C^{14} particle but to one or more others in each collision or nuclear event. While the present imprecise terminology is already hallowed by usage, it seems reasonable, though perhaps deplorable, that better terms might be found. In this spirit, we suggest that one can maintain the focus of one's attention on the C^{14} particle by applying to it the name* archekine (*archein + kinein = prime mover*).

reduced below about 30 kev.; since the electron affinity of C^- is negative, it seems unlikely that carbon more negatively charged than this can exist in the target matrix except where such a carbon fragment is surrounded by positive ions. In general, the electron affinities of doubly or more highly charged negative ions are negative and these ions would furnish the electrons required for the assumption of negative charge by the hot-atom. While the cross sections for ionization and electron excitation are extremely small, the species C^+ could be formed by direct electron exchange processes involving the positive ions of the lattice. Carbon more highly oxidized or reduced than when in the C^+ or C^- states results most likely from *chemical* processes involving the formation of binuclear or more complicated aggregates.

The initial energy possessed by the C^{14} recoil fragment is several thousands of times ordinary chemical bond energies; most of this energy is lost through collisions with or fragmentation of the ions of the target matrix. Occasionally one of these struck ions may thus acquire an energy sufficiently large to produce additional displacements in the lattice.

Libby's Hard-sphere Model

The chemical fate of the C^{14} archekine depends certainly upon the nature of the environment when its energy has been reduced to a level sufficiently low to permit the persistence of chemical combinations or electron displacements. Among other things, the nature of that terminal environment will be influenced by the amount of energy which the hot-atom possessed when trapped effectively by the lattice within some small volume. In an early paper dealing with these matters, Libby (16) assumed that the mean free path of an energetic recoil particle in a simple ionic lattice would be of the order of the mean ionic separation for hard-sphere (billiard ball) type collisions. For example: in beryllium nitride the mean ionic separation is a little over 2 Å* and about 8 hard-sphere collisions with lattice ions are required to reduce the energy of the archekine to the order of 25 ev. The mean separation between the site of production and the site of entrapment is about $2.2\sqrt{8} = 6$ Å. This corresponds to the release of 40 kev. in a volume which contains about 150 ions, an act equivalent to raising the temperature of the region to nearly 10^7 °K. The relaxation time for cooling of such a heated zone would be sufficiently long, about 10^{-9} sec., to permit considerable diffusion to take place. If one assumes that the C^{14} particle is at or near the hottest part of the region, thermal diffusion would tend to increase the influence on it of beryllium ions above that expected from the stoichiometry of the crystal.

The presence in the target of polyatomic lattice units would result in only slight modification of the picture sketched above, in that fragmentation of such ions in the immediate vicinity of the archekine is an energy-lowering phenomenon which must be considered. However, the local temperatures predicted are so high that complete fragmentation of such polyatomic ions would be expected; thus, the initial reactions of the entrapped C^{14} particle would be with atoms or ions of low charge, regardless of whether the target crystal contained simple or complex ions or both.

**Beryllium nitride crystals are of the anti-Tl_2O_3 type, $a = 8.13$; there are 16 Be_3N_2 in the unit cell (25).*

Model Based on Suggestions of Seitz and Koehler

While the collision cross section for archekine – lattice ion encounters may be of the order of the square of twice the mean ionic radius in the crystal when the archekine energy is a few electron volts, it must be much smaller when the energy is hundreds or thousands of electron volts. The model suggested by Libby must be modified in its reference to archekines with energies above, say, 100–200 ev., but seems essentially correct for energies below this range.

At the beginning of its travels in the lattice, the energy of the archekine is sufficiently high that encounters with simple ions are best described by classical Rutherford scattering (20). Small angle collisions are favored and the average energy transferred in a collision is below one electron volt; the hot-atom may be said to produce a *track* in the crystal. Occasionally, a struck ion receives enough energy, about 25 ev. in the case of a well-bound solid (19), to be displaced from its lattice site; detailed consideration shows that the average energy so transferred is of the order of 200 ev. The total collision cross section is of the order of 10^{-17} cm.^{2}, yielding a mean free path of *several tens of Å*. When the energy of the archekine has been reduced to about 6 kev. the collisions become hard-sphere in character.

When the archekine enters the hard-sphere range, its average distance from the site of its production may be several hundred Å; the track which it followed will be surrounded by a cylinder of heated crystal distorted here and there by the appearance of *displacement spikes* (10), spheroidal volumes in which the displaced ion secondaries and their progeny have dissipated their energy to the lattice. In the hard-sphere range, energy transfer is very efficient, 5 or 6 collisions, on the average (16), being sufficient to reduce the energy of a C^{14} hot-atom to 25 ev.; however, the collision cross section does not reach atomic dimensions until the archekine is almost at rest (20). As long as the mean free path is large compared with the mean lattice-ion separation, the motion of the recoil particle is diffusion-like. In Table I are shown some values

TABLE I

MEAN FREE PATH OF HOT-ATOM FOR HARD-SPHERE COLLISIONS; C^{14} IN Be_3N_2(s)

$E_{C^{14}}$ (ev.)	L_s (Å)	L_m (Å)
3000	230	240
1000	62	67
300	20	32
100	9	14
30	5	7

for the hard-sphere range of the mean free path L_s of a carbon hot-atom in the beryllium nitride lattice as computed from equations given by Seitz and Koehler (20). These L_s values are an order of magnitude larger than those one would expect on the basis of calculations by Brinkman (10); the difference arises in the choice of a value to be assigned to a coefficient in the calculation of a screening constant. Seitz and Koehler follow Bohr (9) in selecting a small value. There is indirect experimental evidence that the long mean free paths

calculated by the method of Seitz and Koehler are reasonable, in a now considerable body of experimental data on the collision cross sections of neutral atoms; we assume that the motion of a carbon archekine in an ionic lattice may be likened to diffusion of a neutral atom in a still atomic gas. Using this model one need but estimate the repulsive potential for the hot-atom interaction with the average lattice ion in order to compute a collision cross section, and from it a mean free path. The values of the mean free path L_m based upon H–H_2 (4, 7), He–He (1, 3), He–A (6), and A–A (2, 5, 8) high energy scattering data are given in Table I.

When we consider the slowing down of an archekine in an ionic crystal in which one of the species is polyatomic we see that the properties of this model are very different from those of the Libby hard-sphere model. In this case effective entrapment of the hot-atom is impossible much above energies of the order 100–200 ev.; thus, the amount of energy which can be dissipated to the lattice about such a site is quite modest, and atomization of the polyatomic ions nearby is not to be expected to be anything like complete. Fragmentation of these complex ions will occur, but the scale of the demolition process is of a much lower order than that predicted by Libby's model in which the entire recoil energy of the archekine is released from a very small volume.

As the energy of the archekine falls to a few hundred electron volts, its collision cross section becomes so large that the remainder of its kinetic energy will be dissipated within a compact volume whose radius is of the order of its mean free path, only two or three collisions with lattice ions being left to it. Each of these remaining collisions will produce within the volume mentioned a *hot-spot*, i.e. a region where the archekine and/or displaced secondary (*knock-on*) reach kinetic energies of the order of 25 ev. in coming to rest, or where a struck ion receives a little less than the threshold energy for displacement (20); the energy associated with the hot-spot in which the archekine is finally trapped by the lattice is thus 25–50 ev.

The 25–50 ev. in the terminal hot-spot is, at first, shared by the archekine and a few near neighbors; if 5 particles share this energy, their equivalent temperature is of the order of 10^5 °K. When the radial diffusion of this energy has progressed to the point where a volume about that of a unit cell is involved, the temperature of the region will have fallen to 2500°K., which, for example, is the fusion temperature of beryllium nitride. The chemical fate of the archekine must be determined largely during this cooling period, the relaxation time for which is of the order of 10^{-12} sec. This time is so short that the disorder characteristic of the molten state probably is not achieved except in the center of the hot-spot (20), but some disorder may be entrapped in the freezing process. About one electron volt per ion is tied up in a typical dislocation ring (21) and release of several electron volts from such a source could provide easily the activation energy required for reaction with the solvent of an entrapped archekine close by. If polyatomic ions are present the effective local temperature will be even lower than that calculated above because of the uptake of energy in fragmentation processes.

It is important to note the different possible effects of diffusion-like processes occurring before freezing of the hot-spot which would be predicted from the

Libby and Seitz–Koehler models. In the former case, where the archekine is trapped within a small volume at the very outset, a given kind of rate process would have many chances to occur in the 10^{-9} sec. lifetime of the region; in such a situation thermal equilibrium would be attained over quite an appreciable volume, and ions relatively far from the archekine might diffuse to it before cryosis set in. The Seitz–Koehler model of the process leads to the prediction that only a small part of the original energy of the archekine is available in the terminal hot-spot, and a given kind of rate process would have only a few chances to occur in the 10^{-12} sec. lifetime of the region; in such a situation thermal equilibrium is established over a volume containing only 5 or 10 ions, and only near neighbors of the archekine could diffuse to it before solidification of the hot-spot.

CHEMICAL PROCESSES

As has been mentioned above, the specifically chemical consequences of these two different final environmental situations would likely be quite similar for simple ionic targets. We would expect different chemical phenomena to occur were the targets molecular crystals or ionic solids containing molecular ions. As an example, consider the target ammonium bromide. Production of a long-lived, high temperature hot-spot would likely involve the complete demolition of ammonium ions in the vicinity of the hot-atom; as cooling occurred, competitive reactions among C, N, Br, and H would determine the spectrum of chemical species observed upon solution of the target. Where a short-lived, low temperature hot-spot is produced, only partial fragmentation of ammonium ions is possible energetically; upon cooling, competitive reactions among C, H, and fragments such as NH, NH_2, and NH_3^+ would determine the distribution of radiocarbon over various chemical forms upon solution of the irradiated material. The Libby model results in a concentration of energy sufficient to permit the formation of H^+ which might tend to oxidize the archekine; the Seitz-Koehler model predicts that much less energy than this will be available and, since it costs about one electron volt less to remove a hydrogen atom from an ammonium ion than to remove a proton (23, 26), the hydrogen made available would tend to reduce the carbon archekine.

In simple ionic crystals where the nature of the target is such that few carbon-containing aggregates can be formed and where only one or two kinds of terminal hot-spot environment can come into being, the amount of energy actually available in the terminal hot-spot may exert a critical influence upon the final chemical state of the archekine trapped there; in fact, the distribution of product radiocarbon over various oxidation states for such targets may be a simple reflection of the distribution of terminal hot-spot energies. For more complex systems, the Libby and Seitz-Koehler models again predict different results. Because of the long life of its kind of hot-spot, one would expect from the Libby model some dependence of the final chemical state distribution upon the recoil energy of the hot-atom (at the 10^3–10^5 ev. level); in the Seitz–Koehler model no processes have chemical significance before entrapment of the archekine (at the 10–100 ev. level), so no effect of recoil energy variation should be noted provided that energy was always

higher than the highest possible entrapment energy. In this regard it is interesting to note the results obtained by Schuler (24) and by Holmes and McCallum (13). Schuler studied the retention in liquid methyl and ethyl iodides of iodine activated by the processes (d, p), $(n, 2n)$, and (γ, n) and observed the same retentions as in radiative neutron capture (15); Holmes and McCallum obtained similar results when the retention of copper in solid copper salicylaldehyde-*o*-phenylenediimine after the process (γ, n) was compared with the effect of the (n, γ) reaction (11).

It may be difficult to unravel the effects of nature of target material and solvent. Where the ion charges in a simple ionic crystal target are not very different we would expect carbon hot-atoms to come to rest in terminal hot-spots exhibiting a more or less symmetrical distribution of oxidizing and reducing characters. This should result in a similarly symmetrical distribution of product radiocarbon among various oxidation states, provided that reactions of the entrapped radicals with the solvent are not entirely of one character; for water solvent, since both its oxidation and reduction can be effected, one should be able to see little modified the oxidation state distribution of the radiocarbon in the terminal hot-spots.

RADIOCARBON PRODUCT DISTRIBUTION

In Table II are collected the results of recently completed chemical fractionation studies of the radiocarbon compounds resulting from the solution in

TABLE II

DISTRIBUTION OF RADIOCARBON AMONG VARIOUS FINAL PRODUCTS

Oxdn. No.	Carrier	Target						
		$(NH_4)_2SO_4$	Be_3N_2	NH_4Br	$NaNO_3$	Na_2CO_3	$NaHCO_3$	NaOOCH
	CO_2	39.5	14.4	1.7	98	22	22	4
	$CO(NH_2)_2$	7.3	6.2	0.4				
+4	$CNH(NH_2)_2$	0	18.7	0				
	$CN(NH_2)$		4.6					
+3	$(COOH)_2$					39	40	6
	CO	2.0	0.06	1.3	0	1	1	5
	HCOOH	15.5	8.3	1.3		3	4	15
+2	HCN	3.9	6.5	2.0				
	HOOCCHO					24	24	11
+1	$HOCH_2COOH$					10	10	31
	HCHO	13.2	2.4	5.8		0		1
0	HOH_2CCHO							14
$-\frac{1}{2}$	OHCCHO							15
	CH_3OH	0.7	0.15	0.4		0		
	CH_3NH_2	16.1	4.1	79	0			
−2	CH_3NHNH_2		11.2	0				
	CH_3Br			1.8				
−4	CH_4	0.5	25.8	7.5	0			

water of a number of irradiated ionic crystal targets. For the systems ammonium sulphate (28), ammonium bromide (30), beryllium nitride (29), and sodium nitrate (31), the nuclear reaction is $N^{14}(n, p)C^{14}$ and the initial archekine energy is 40 kev.; for the systems sodium carbonate (22), and sodium bicarbonate and formate (17), the nuclear reaction is $C^{12}(\gamma, n)C^{11}$ and the initial archekine energy under the irradiation conditions employed was about 0.5 Mev.

The sodium carbonate and ammonium chloride oxidation state distributions, the former peaking in the positive oxidation number range, the latter in the negative, indicate the relatively subsidiary role of the water solvent and the controlling nature of the terminal environment of the archekine; the relative inertness of the bromide and sodium ions is also reflected by the data.

The distribution of radiocarbon products in the beryllium nitride study confirms the expectation mentioned above concerning a symmetrical distribution of product radiocarbon among various oxidation states. An especially important result of the product distributions observed there and in the (γ, n) systems is that they furnish evidence that the skeletons of complex chemical species are formed and persist in the irradiated crystals; there seems to be no mechanism other than formation in the lattice which accounts satisfactorily for the appearance of skeletal types such as C—C, $NC(N)_2$, NCN, CN, and CNN among the final products. In this regard, the formation of methylhydrazine is important because it is the only nitrogenous species in which the oxidation number of N is different from -3 (that of ammonia and nitride ion); this compound may thus be a relic of a C–N electron transfer reaction. Another important feature of the beryllium nitride target results is that the oxidation state distribution peaks at the extremes rather than near neutral carbon. Thus it appears that the several oxidation states are not reached by random walks among adjacent oxidation states.

In ammonium sulphate, hydrogen and oxygen are present in the same ratio as in the solvent; ammonium bromide and sodium carbonate each contain but one element of water; and beryllium nitride contains neither. Table III

TABLE III

PER CENT OF RADIOCARBON VALENCES UTILIZED BY H, O, N, OR C^{12}

Bonded atom	Target						
	$(NH_4)_2SO_4$	Be_3N_2	NH_4Br	$NaNO_3$	Na_2CO_3	$NaHCO_3$*	NaOOCH*
H	24.9	41.3	71.3		5.8	6.5	22
O	63.3	24.4	6.4	98	74.8	76	60
N	10.7	34.3	21.2				
C^{12}					19.5	18.5	19

**At the time this paper is being prepared, degradation information on the two-carbon products in these target systems is not available. In making these rough calculations a random distribution of the radioisotope has been assumed.*

is a compilation for these and other target crystals of the per cent of radiocarbon valences in the final product state utilized by H, O, N, or C^{12}. To this

table we make the following annotations: (1) the ammonium bromide and sodium carbonate data show very good correspondence in the reactivities of the simple ion, central atom, and outer atom in each case; (2) comparison of the ammonium sulphate and beryllium nitride data indicates the powerful scavenging character of crystal oxygen as compared with water oxygen; (3) the shift in the sodium formate oxidation state distribution to a less positive peak compared with that of sodium carbonate is reflected in the sharp increase of bonds to hydrogen, and the lack of change in the carbon bonding percentage is probably an indication that C—C bonds are formed early in the lifetime of a terminal hot-spot when partially stripped carbon atoms are available; it is surprising that the sodium bicarbonate data resemble those for sodium formate in view of the availability of hydrogen in the crystal.

Only in the case of ammonium sulphate, among the nitrogenous targets, are all of the kinds of atoms found in the products present in the target substance; even so, there is no direct correlation between the thermodynamic stability of the several products and their final abundances in the solution of the target. This is probably an indication that, as in the case of beryllium nitride, only parts of the final molecules are stable in the target. Alternatively, the relative rates of competitive reactions with the solvent may determine the distribution of radiocarbon among several forms with the same carbon oxidation number.

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A SYNTHESIS OF 5-*O*-METHYL D-GLUCOSE AND OF 2-*O*-METHYL D-GLYCERONAMIDE[1]

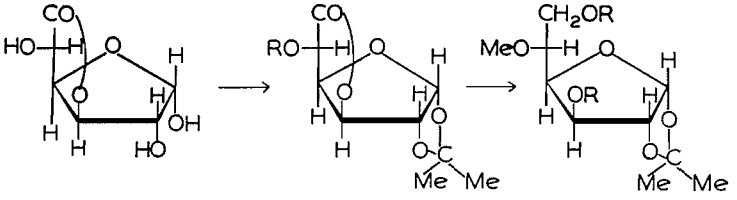
By J. K. N. Jones

ABSTRACT

A preparation of 5-*O*-methyl D-glucose from 1,2-*O*-*iso*propylidene D-glucurone is described. Oxidation of the D-glucose derivative with periodate gave 2-*O*-methyl D-glycerose from which 2-*O*-methyl D-glyceronamide was prepared.

INTRODUCTION

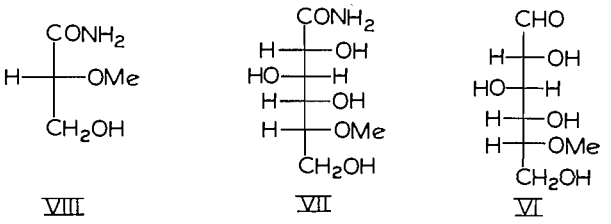
The reference compound 2-*O*-methyl D-glyceronamide (VIII) was required. Its preparation from a suitably substituted derivative of D-glucose was considered to be feasible and, accordingly, the preparation of 5-*O*-methyl D-glucose (VI) was undertaken. This compound had been prepared earlier (3) from D-glucose. The ready availability of D-glucurone made this substance a more attractive starting material. D-Glucurone (I) condenses with acetone to give the well-characterized 1,2-*O*-*iso*propylidene derivative (II) which possesses a free hydroxyl group on C-5. Previous workers (2) had indicated that this material could not be methylated with Purdies' reagents without decomposition. It was observed that when water was rigorously excluded and if the reaction was carried out in the presence of anhydrous calcium sulphate methylation proceeded in the normal manner. The resultant 5-*O*-methyl



I

II, R=H
III, R=Me

IV, R=H
V, R=CO.CH$_3$



VIII VII VI

derivative (III) on reduction with lithium aluminum hydride in ether gave 1,2-*O*-*iso*propylidene 5-*O*-methyl D-glucose (IV) which was characterized as its crystalline 3,6-di-*O*-acetyl derivative (V). Hydrolysis of this material gave 5-*O*-methyl D-glucose (VI), a sirup which on oxidation with bromine water yielded 5-*O*-methyl D-gluconic acid, characterized as the crystalline amide (VII). Oxidation of this product with periodic acid resulted in the formation of 2-*O*-methyl D-glycerose. Attempts to isolate this material by

[1]*Manuscript received November 28, 1955.*
Contribution from the Department of Chemistry, Queen's University, Kingston, Ontario.

extraction with either chloroform or ether were unsuccessful. Accordingly the aldehyde was oxidized *in situ* with bromine and the resultant glyceronic acid derivative converted first to the ester and then to the required amide (VIII). The racemic amide was prepared previously by Baker (1), and has a lower melting point, 71°C. compared with 87°C. The analytical values for methoxyl are likely to be unreliable as reported by Baker (1).

EXPERIMENTAL

The following solvents (v/v) were used to separate sugars on paper chromatograms: (A) ethyl acetate: acetic acid: formic acid: water—18: 3: 1: 4; (B) butan-2-ol: pyridine: water—10: 3: 3. Solvents were removed by evaporation at 40°C. or less and optical rotations were determined at 20 ± 2°C. and in water unless otherwise stated.

1,2-O-iso-Propylidene 5-O-Methyl D-*Glucurone*

1,2-*O-iso*-Propylidene D-glucurone (7 gm.) (II) was converted to the 5-*O*-methyl ether by methylating it with Purdies' reagents in the presence of drierite. The product, which was isolated in the usual manner, was a sirup which was purified by distillation, b.p. 140–145°C. at 0.01 mm. (bath temp.), $n_D^{29°}$ 1.4690, yield, 4.7 gm.; $[\alpha]_D$ 48° (*c*, 0.9). The lactone gave with alcoholic ammonia an amide, m.p. 174°C., $[\alpha]_D$ −29° (*c*, 2.5). Anal.: Calc. for $C_{10}H_{17}O_6N$: C, 48.7; H, 6.9; N, 5.7; OMe, 12.6. Found: C, 48.7; H, 6.7; N, 5.7; OMe, 14.5.

The lactone derivative on hydrolysis with dilute formic acid yielded 5-*O*-methyl D-glucurone which moved at 1.35 times the speed of rhamnose in solvent (A).

1,2-O-iso-Propylidene 5-O-Toluene-p-sulphonyl D-*Glucurone*

1,2-*O-iso*-Propylidene D-glucurone (1 gm.) was dissolved in pyridine (10 ml.) and toluene-*p*-sulphonyl chloride (1 gm.) was added. The solution became warm and, after the initial reaction was over, was allowed to stand at room temperature for a day. The reaction mixture was poured on to ice when the crystalline 5-*O*-toluene-*p*-sulphonyl derivative separated. It was collected on the filter, washed well with water, and recrystallized from methanol or aqueous acetone, m.p. 189°–194°C. not changed on further recrystallization, $[\alpha]_D$ 84° (*c*, 0.44 in acetone.) Anal.: Calc. for $C_{16}H_{18}O_8S$: C, 52.0; H, 4.9; S, 8.7. Found: C, 52.0; H, 4.8; S, 8.5. The product dissolved in aqueous alkali with the formation of an intense yellow color.

1,2-O-iso-Propylidene 5-O-Methyl D-*Glucose* (*IV*)

1,2-*O-iso*-Propylidene 5-*O*-methyl D-glucurone (4.4 gm.) was reduced by adding its solution in ether (25 ml.) to a solution of lithium aluminum hydride (4 gm.) in ether (25 ml.). The glucose derivative was isolated from the neutralized and filtered solution by extracting it continuously with chloroform. The sirupy product was purified by distillation, b.p. 160°C. (bath temp.) at 0.1 mm., $[\alpha]_D$ −8° (*c*, 1.0), yield, 4.1 gm. Anal.: Calc. for $C_{10}H_{14}O_6$: C, 52.2; H, 6.1; OMe, 13.5. Found: C, 52.2; H, 6.25; OMe, 13.7. Acetylation of the product with pyridine and acetic anhydride yielded the known crystalline 3,6-di-*O*-acetyl derivative (4.0 gm.) (V), m.p. 87°C. after recrystallization from

ligroin (b.p. 60–80°C.). Anal.: Calc. for $C_{14}H_{22}O_8$; C, 52.9; H, 7.0; OMe, 9.8. Found: C, 52.5; H, 7.0; OMe, 9.9. Pure 1,2-*O*-*iso*propylidene 5-*O*-methyl D-glucose was recovered from the diacetate after it had been deacetylated with *N* sodium hydroxide solution.

5-O-Methyl D-*Glucose* (*VI*)

1,2-*O*-*iso*-Propylidene 5-*O*-methyl D-glucose (2.0 gm.) was hydrolyzed with 0.1 *N* sulphuric acid (20 ml.) at 100°C., $[\alpha]_D$ $-8° \rightarrow -3°$ (constant value, 1 hr.). The sirupy product (1.77 gm.) was isolated after removal of the sulphuric acid as barium sulphate. Its rate of movement relative to that of rhamnose was 1.1 (in solvent A) and 1.2 (in solvent B). It was converted, without purification, to 5-*O*-methyl D-gluconic acid by oxidizing it with bromine water in the usual manner. Excess of bromine was removed by aeration when chromatographic examination of the solution (solvent B) showed that reducing sugar was absent. Hydrobromic acid was removed with silver carbonate and the solution filtered. The acid, isolated by the usual procedure, was converted to the lactone, which crystallized. This product was difficult to purify. The crude material, which had m.p. 130°C., was converted to the amide (VII) by saturating its solution in methanol with ammonia. The amide was recrystallized either from water or from methanol, m.p. 150°C., and had $[\alpha]_D$ 25° (*c*, 0.14) and therefore obeys Hudson's amide rule. Its rate of movement was identical with that of glucose in solvent (B). Anal.: Calc. for $C_7H_{15}O_6N$: C, 40.0; H, 7.2; N, 6.7; OMe, 14.9. Found: C, 40.2; H, 7.4; N, 6.2; OMe, 15.0.

Oxidation of 5-O-Methyl D-*Gluconamide with Periodate*

The amide (VII) (0.7 gm.) was dissolved in water (10 ml.) and oxidized with paraperiodic acid (0.7 gm.) at 24°C. during 24 hr. In a trial experiment attempts to isolate 2-*O*-methyl D-glycerose were unsuccessful. Accordingly bromine was added to the reaction mixture and the oxidation was allowed to proceed for 48 hr. Excess of bromine was then removed by aeration and the solution was neutralized with barium carbonate and filtered. The filtrate was shaken with silver carbonate, filtered, and silver ions removed from solution as silver sulphide. The filtered solution was then concentrated to a sirup which was boiled with methanolic hydrogen chloride for six hours in order to esterify the glyceronic acid derivative. The 2-*O*-methyl D-glyceronamide (VIII) was prepared from the resultant ester in the usual manner. Yield, 60 mgm. of white crystals, m.p. 86–87°C., $[\alpha]$ 71°±4° (*c*, 0.7 in methanol). Anal.: Calc. for $C_4H_9O_3N$: C, 40.3; H, 7.56; N, 11.8; OMe, 26.1. Found: C, 40.2; H, 7.6; N, 11.9; OMe, 26.7.

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ON FLAME PROPAGATION IN EXPLOSIVE MIXTURES OF GASES

I. GENERAL THEORY[1]

By Robert Sandri[2]

ABSTRACT

The system of differential equations of flame propagation is set up and discussed. It is shown that, without any major influences being neglected, the energy equation can be reduced to the form

$$\zeta\left(\frac{d\zeta}{d\eta}+1\right) = \phi(\eta)$$

with the boundary conditions

$$\zeta = 0 \text{ for } \eta = 0 \text{ and for } \eta = 1.$$

Some qualities of the solutions of this equation are discussed and a simple numerical method of solution is described. The flame velocity V_0 is found as an eigenvalue of the energy equation. The temperature distribution in the flame zone can then be found by an ordinary quadrature. Further, an approximation formula for finding V_0 directly is derived

$$V_0 = \frac{1}{1-\eta_m}\left[2\int_0^1 F(\eta)d\eta\right]^{\frac{1}{2}}$$

where $F(\eta)$ is proportional to $\phi(\eta)$ and has a maximum for $\eta = \eta_m$.

1. INTRODUCTION

The processes involved in the propagation of flames in explosive mixtures of gases are very complex and an exact mathematical description of them is very difficult. It is true that with the help of electronic computers even highly complex systems of equations can be solved but some simplification is still desirable. In the first place, it is always interesting and useful to show up regularities and laws of nature underlying the great apparent complexity of the problem. Moreover, an entirely exact mathematical treatment is in most cases useless because the available kinetic data are incomplete and not entirely reliable.

On the other hand, the purpose of the theory sets a limit to simplification. It cannot be the primary object of a theory of flame propagation to calculate the flame velocity. This quantity can be measured rather easily and is well known in most cases. The principal purpose of the theory, on the contrary, should be to utilize this knowledge for obtaining information regarding kinetic data by comparison of the computed and observed values of flame velocity. If such conclusions are to be convincing and reliable, mathematical and physical simplification must not be exaggerated.

An exact theory of flame propagation has been worked out by Hirschfelder and his collaborators (3, 4, 5, 6, 7) and has been successfully applied to several cases of combustion. However, Hirschfelder's method requires a great many

[1]*Manuscript received October 17, 1955.*
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difficult computations. Recently, Kármán and Penner have shown that it is possible to simplify computations a great deal without losing much accuracy (11).

In the present paper an attempt is made to establish a theory which does not neglect any major influences acting in the phenomenon of flame propagation and at the same time is mathematically quite simple. It has been found to yield results which differ only by a few per cent from the results obtained by the exact method of Hirschfelder *et al.* while it is still simpler than the method of Kármán and Penner. Moreover, it involves a transformation which is universally applicable and is interesting from a theoretical point of view.

2. THE DIFFERENTIAL EQUATIONS OF FLAME PROPAGATION

Let us suppose that an explosive mixture of several gases is moving in the direction of the positive x-axis at such a speed that the flame zone remains motionless relative to the co-ordinate system. We shall consider the one-dimensional, steady-state process only which practically does not involve any restriction to generality. Let V be the average mass rate of flow at any point and ρ the specific mass. Then an equation for the conservation of mass applies, namely

$$[1] \qquad \rho V = M = \text{const.} = \rho_0 V_0 = \rho_f V_f$$

where the subscript 0 refers to the initial mixture and the subscript f to the flame gases, i.e., to the burned mixture.

Now let us consider the equation expressing the conservation of energy. Disregarding kinetic energy, viscosity, and thermodiffusion, we have

$$[2] \qquad \frac{d}{dx}\left(\lambda \frac{dT}{dx}\right) - \frac{d}{dx}\sum_i n_i m_i (V + V_i) H_i = 0.$$

Here, λ is the heat conductivity, T is the absolute temperature, n_i and m_i are the concentration (moles per cm.^{3}) and the molecular weight of the component i of the mixture, H_i is the enthalpy per unit mass, and V_i is the velocity of diffusion flow of the same component.

Further, there is a set of equations of continuity for all components

$$[3] \qquad \frac{d}{dx}[n_i(V + V_i)] = U_i$$

where U_i is the rate of production of the component i (moles per cm.^{3} per sec.) due to chemical reactions.

So far, our assumptions have been identical with those made by Hirschfelder *et al.* However, the above equations can be lumped together and greatly simplified as follows. Evidently

$$[4] \qquad \sum_i m_i H_i U_i = -Q,$$

Q being the heat developed by chemical reactions per second and cm^3. Furthermore

$$[5] \qquad \sum_i n_i m_i V \frac{dH_i}{dx} = V \frac{dT}{dx} \sum_i n_i m_i c_{pi} = M c_p \frac{dT}{dx}$$

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where c_p is the specific heat per unit mass of the mixture, at constant pressure.

Transforming the second term in equation [2] by means of equations [3], [4], and [5], we find

$$[6] \qquad \frac{d}{dx}\left(\lambda \frac{dT}{dx}\right) - Mc_p \frac{dT}{dx} + Q - \frac{dT}{dx}\sum_i n_i m_i V_i c_{pi} = 0.$$

From the definition of V it is clear that

$$\sum_i n_i m_i V_i = 0.$$

Hence, the last term in equation [6] will be very small compared to the other terms as long as the specific heats of the components of the mixture do not differ too much. Disregarding the last term, we obtain the energy equation in the form which has been used by many authors, e.g., Boys and Corner (1), Jost (8), Kármán and Millán (10), Lewis and Elbe (13), Roy (15), Semenov (16), Tanford (17), Zeldovitch and Frank-Kamenetzky (18). The discussion given here and numerical evaluation show that this simplified form will be applicable with a very good approximation in most practical cases, except for mixtures rich in hydrogen. (If hydrogen is present in low concentration, it does not contribute appreciably to the last term in equation [6]. It may, of course, play a very important role in the reaction mechanism and thus affect Q a great deal.) However, there is no need of neglecting the last term and no substantial complication is introduced by keeping it, as we shall presently see.

An expression for V_i is needed in order to evaluate equations [3] and [6]. According to Hirschfelder and Curtiss (3), we can place

$$[7] \qquad V_i = -\frac{D_i}{y_i}\frac{dy_i}{\omega x}$$

where y_i is the mole fraction of the component i and D_i can be calculated, with a very good approximation, by the formula

$$D_i = \left(1 - \frac{n_i m_i}{\rho}\right) \Big/ \sum_{k \neq i} \frac{y_k}{\mathfrak{D}_{ik}},$$

$\mathfrak{D}_{ik}$ being the ordinary binary diffusion coefficient of the components i and k.

In order to obtain a system of working equations, it is useful to place

$$[8] \qquad z = \frac{\lambda}{Mc_p}\frac{dT}{dx}$$

$$[9] \qquad \delta_i = \frac{\rho c_p D_i}{\lambda}$$

$$[10] \qquad m = \rho / \sum_i n_i = \sum_i y_i m_i.$$

The reduced diffusion coefficients δ_i are dimensionless quantities and m is the average molecular weight of the mixture.

Then, equation [6] assumes the form

$$[11] \qquad z\frac{dz}{dT} = \omega z^2 + z - \varphi$$

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where

$$\omega = \frac{1}{c_p}\frac{dc_p}{dT} + \sum_i \delta_i \frac{m_i c_{pi}}{mc_p}\frac{dy_i}{dT} \quad [12]$$

$$\varphi = \frac{\lambda Q}{M^2 c_p^2}. \quad [13]$$

From [3] and [7] we obtain

$$z\frac{d}{dT}\left(\frac{\delta_i}{m} z \frac{dy_i}{dT} - \frac{y_i}{m}\right) + \psi_i = 0 \quad [14]$$

where

$$\psi_i = \frac{\lambda U_i}{M^2 c_p}. \quad [15]$$

If complete kinetic and physical data are available, ω, φ, and ψ_i are known as functions of T and y_i and dy_i/dT. Then equations [11] and [14] are sufficient to determine all y_i and z as functions of T. The initial concentrations y_{i0} are supposed to be known and the concentrations in the burned mixture y_{if} can be calculated from them.* Moreover, z must be zero at the hot boundary ($T = T_f$). Some controversy exists as to the assumption to be made for z at the cold boundary ($T = T_0$). However, as pointed out by Richardson (14), there can be little doubt that no appreciable error is introduced by assuming that $z_0 = 0$. This last boundary condition is supernumerary and makes it possible to determine M (or $V_0 = M/\rho_0$) as an eigenvalue of the problem.

3. THE REDUCED ENERGY EQUATION

The exact solution of the system of differential equations is a very difficult task even if the system of chemical reactions is rather simple. However, in most cases this task can be greatly simplified.

In the first place, one of the differential equations [14] can always be discarded because

$$\sum_i y_i = 1.$$

Further, it is often admissible to assume that the enthalpy of the mixture remains reasonably constant throughout the flame zone because the energy transport by diffusion is opposite in direction and approximately equal in size to the energy transport by heat conduction so that these two influences more or less cancel each other. This assumption was made by Lewis and Elbe (12), by Semenov (16), and by Zeldovitch and Frank-Kamenetzky (18). It has also been backed by Jost (9), by Hirschfelder (2), and by Kármán and Penner (11). It allows another of the differential equations of the system to be discarded.

However, other hypotheses often give better results. Very often, chemical reactions are confined to a comparatively narrow range of temperature near T_f. Then, as Kármán and Penner have shown, series expansions can be used

*The values of dy_i/dT at the hot boundary, which are also needed, can be found by series expansion at $T = T_f$, with $(dy_i/dx)_f = 0$.

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for the mole fractions y_i of which only the first terms need be considered. Thus, the y_i can easily be determined from equations [14] as functions of T in the interval near T_f and the system is reduced to the one equation [11] whose solution gives the eigenvalue V_0.

Stoichiometric relations and pre-established equilibria may also help to the same end. These methods will be further discussed in the applications of the general theory. Here, we shall assume that, by any of the methods referred to above, all y_i have been determined as functions of T.

Normally, the variables ω and φ, as defined by [12] and [13], are then also known as functions of T and equation [11] can be used to solve the problem completely.

Equation [11] is amenable to considerable simplification. To this end, we introduce the dimensionless variables

$$E = \exp\left(\int_T^{T_f} \omega \, dT \right) \tag{16}$$

$$\zeta = \frac{zE}{K} \tag{17}$$

$$\eta = \frac{1}{K} \int_T^{T_f} E \, dT \tag{18}$$

$$\phi = \frac{\varphi E}{K} . \tag{19}$$

The constant K is defined as

$$K = \int_{T_0}^{T_f} E \, dT. \tag{20}$$

Then, equation [11] assumes the form

$$\zeta \left(\frac{d\zeta}{d\eta} + 1 \right) = \phi \, (\eta) \tag{21}$$

with the boundary conditions

$$\zeta = 0 \text{ for } \eta = 0 \text{ (hot boundary)}$$

$$\zeta = 0 \text{ for } \eta = 1 \text{ (cold boundary).}$$

By equation [18] η is given as a function of T. All quantities known as functions of T, i.e., λ, c_p, y_i, and ϕ, are therefore also known as functions of η.

Equation [21] can be called the reduced energy equation. Methods for its integration and for the determination of the eigenvalue V_0 are given in Section 5.

When ζ has been determined as a function of η, the temperature distribution in the flame zone can be found, according to [8], [17], and [18], by the formula

$$x = \frac{1}{M} \int \frac{\lambda dT}{c_p z} = \frac{1}{M} \int \frac{\lambda d\eta}{c_p \zeta} . \tag{22}$$

Frequently, the last term in [6] can be neglected and c_p can be considered as

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constant. In this case, we have $\omega = 0$ and $E = 1$ and the substitutions [17], [18], and [19] assume the simple form

[17a] $$\zeta = \frac{z}{T_f - T_0}$$

[18a] $$\eta = \frac{T_f - T}{T_f - T_0}$$

[19a] $$\phi = \frac{\varphi}{T_f - T_0}.$$

Equation [21] with its boundary conditions and equation [22] remain unchanged.

Some complications may arise in the presence of equilibria because terms approaching the indeterminate form $\infty \times 0$ may appear in the expression for φ. It is then necessary to eliminate them by means of any of the equations [14]. The result can again be reduced to the standard form [21], with the same boundary conditions, by substitutions similar to formulae [16] to [20].

4. THE SOLUTIONS OF THE REDUCED ENERGY EQUATION

Equation [21] is known in mathematics as Abel's Differential Equation of the Second Type. Its integration by a finite expression is, in general, not possible but some statements can be made on the behavior of its solutions which, of course, depends solely on the function $\phi(\eta)$.

We shall assume for our discussion that η is a monotonic function of T and that ζ is always positive. This is certainly the case in the absence of such equilibrium reactions which would lead to indeterminate forms which would have to be eliminated (see equations [18], [17], and [8]).

The function ϕ is known from kinetic data save for the factor $1/V_0^2$ (see equations [19] and [13]). Evidently

$$\phi = 0 \text{ for } \eta = 0 \quad (T = T_f).$$

Under normal circumstances, all chemical reactions can be neglected for low temperatures up to a certain temperature T_s. So we have

$$\phi \equiv 0 \text{ for } \eta \geqslant \eta_s,$$

η_s being the value of η corresponding to T_s. Then, the general solution of [21] is

$$\zeta = C - \eta \text{ for } \eta \geqslant \eta_s.$$

For further discussion we shall confine ourselves to the family of solutions which satisfy the first boundary condition

$$\zeta = 0 \text{ for } \eta = 0.$$

This condition leaves no indefinite integration constant but the solutions still differ by the values chosen for V_0. The curves are shown in Fig. 1 for the

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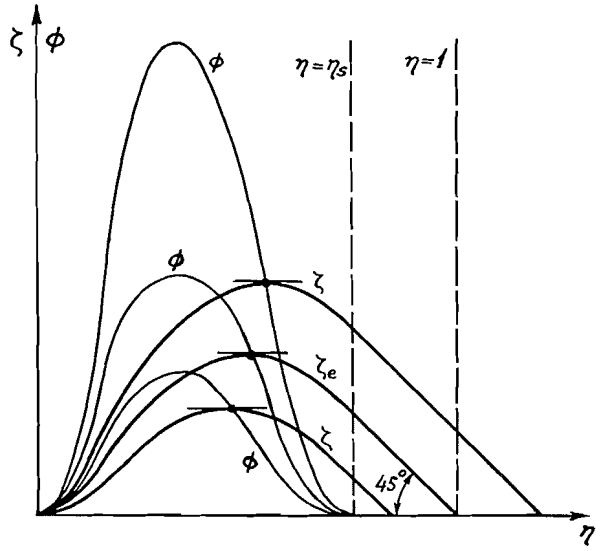

FIG. 1. Solutions of the reduced energy equation.

simplest case, namely, if ϕ is always positive. One of these curves ζ_e, for a particular value V_{00} of V_0, will satisfy also the second boundary condition

$$\zeta = 0 \text{ for } \eta = 1 \quad (T = T_0)$$

and is therefore the real solution of our problem.

For small values of η, $d\zeta/d\eta$ must be positive, otherwise ζ would become negative. Hence, for small η,

$$\zeta = \frac{\phi}{(d\zeta/d\eta)+1} < \phi.$$

From this formula it is evident that ζ increases with η as long as it is smaller than ϕ. Then, for a certain value of η, it becomes equal to ϕ and at the same time has a maximum value because $d\zeta/d\eta$ must be zero at this point. With η increasing further, ϕ decreases and finally becomes identically zero so that, for $\eta \geqslant \eta_s$, the ζ-curve coincides with one of the straight lines $\zeta = C-\eta$. The value of C depends on V_0 and we have only to find that particular value V_{00} for which C is equal to unity so that the second boundary condition is satisfied. Thus the eigenvalue V_{00} can be found by trial and error.

The physical interpretation of these mathematical facts is clear enough. A given burned mixture could have been obtained from quite different initial mixtures of the same components of appropriate initial temperatures. It is by these very initial conditions that the flame velocity is determined. Now, only for one particular value V_{00} we find $C = 1$ and hence $\zeta = 0$ for $\eta = 1$. Otherwise, ζ becomes zero for a value of η other than unity. This means that for a value of V_0 different from V_{00} the composition of the unburned mixture is

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different from that assumed originally and hence also the initial temperature is different.

The function ϕ may be positive in the whole interval between 0 and η_s but it may also change its sign. In this case, since ζ is always positive, we have

$$d\zeta/d\eta = -1 \text{ for } \phi = 0$$

$$d\zeta/d\eta < -1 \text{ for } \phi < 0.$$

Only in the immediate vicinity of $\eta = 0$, ϕ must be positive.

5. INTEGRATION OF THE REDUCED ENERGY EQUATION

The following method is recommended for the numerical integration of equation [21]. Integrating over an interval from η_1 to η_2 we obtain

$$[23] \qquad \tfrac{1}{2}\zeta_2^2 - \tfrac{1}{2}\zeta_1^2 + \int_{\eta_1}^{\eta_2} \zeta d\eta = \int_{\eta_1}^{\eta_2} \phi(\eta) d\eta = \tfrac{1}{2}\Delta Y.$$

Now we make the interval $\eta_2 - \eta_1 = \Delta\eta$ so small that the "Trapezoidal Rule" can be applied to the integral on the left-hand side. So

$$\tfrac{1}{2}\zeta_2^2 - \tfrac{1}{2}\zeta_1^2 + \tfrac{1}{2}(\zeta_2 + \zeta_1)\Delta\eta = \tfrac{1}{2}\Delta Y$$

$$[24] \qquad \zeta_2 = -\tfrac{1}{2}\Delta\eta + \sqrt{[(\zeta_1 - \tfrac{1}{2}\Delta\eta)^2 + \Delta Y]}.$$

By means of this formula, ζ can be computed step by step. The numeric calculation must be repeated with different values of V_0 until both boundary conditions are satisfied. The differences ΔY can be computed once for all and need only be changed by the factor $1/V_0^2$ for each run. On the other hand, the evaluation of formula [24] has to be repeated completely for each run but it is very simple and involves only additions and subtractions if a table of squares is used, in case no electronic computers are available.

Nevertheless it is desirable to derive a formula which makes it possible to dispense with the repeated numerical integration and to find V_{00} directly. To this end, we integrate both sides of equation [21] from $\eta = 0$ to $\eta = 1$. Then, for that solution ζ_e which satisfies both boundary conditions, we obtain

$$[25] \qquad \int_0^1 \zeta_e \, d\eta = \int_0^1 \phi_e \, d\eta = A.$$

Geometrically this means that the area A below the curve representing the real solution ζ_e of our problem must be equal to the area below the corresponding ϕ_e-curve. Now let

$$[26] \qquad V_0^2 \phi(\eta) = V_{00}^2 \phi_e(\eta) = F(\eta).$$

Since $\phi(\eta)$ is proportional to $1/V_0^2$, the function $F(\eta)$ does not contain this factor and is therefore completely known. Then

$$V_{00}^2 = \frac{1}{A} \int_0^1 F(\eta) d\eta.$$

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This formula can serve for computing V_{00} if the area A is known. In order to find A exactly, we should first have to find ζ_e as a function of η by repeated numerical integration. However, a very good approximate value for A can be found directly, because of our knowledge of the general qualities of the ζ_e-curve.

We shall at first assume that the function $F(\eta)$ is zero in the entire interval between 0 and 1, save for a narrow range of η on either side of η_m where $F(\eta_m)$ is a maximum so that

[27] $$\left(\frac{dF}{d\eta}\right)_{\eta_m} = 0.$$

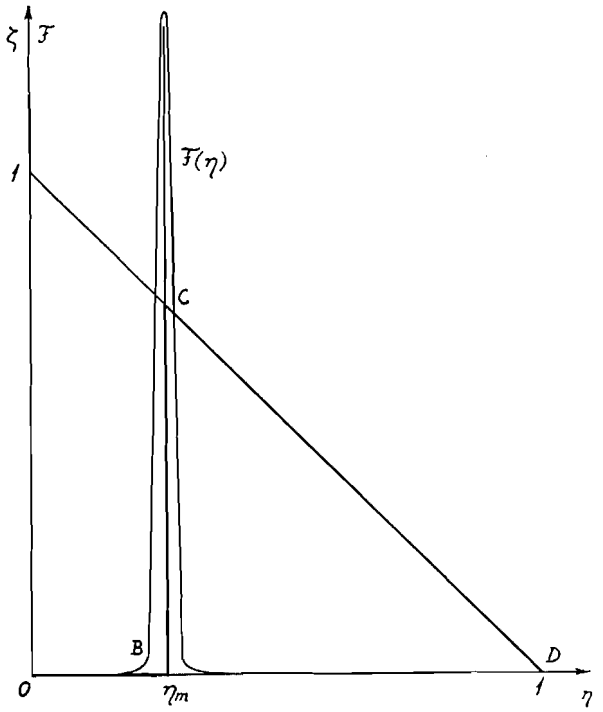

FIG. 2. Solution for a sharply peaked function $F(\eta)$.

Then, according to what has been said in the preceding section, the ζ_e-curve will approach the broken line OBCD (see Fig. 2), so that

$$A = \tfrac{1}{2}(1-\eta_m)^2.$$

Since no iteration is involved in the new formulae, we can now replace V_{00} by V_0. Thus we have

[28] $$V_0 = \frac{1}{1-\eta_m}\left[2\int_0^1 F(\eta)d\eta\right]^{\frac{1}{2}}.$$

This formula yields amazingly good values for V_0 even if the $F(\eta)$-curve is not as sharply peaked as shown. For instance, for the combustion of a stoi-

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chiometric mixture of methane and air, we find $V_0 = 40.4$ cm./sec. while repeated numerical integration of equation [21] gives 40.8 cm./sec. The error is therefore only 1% although $F(\eta)$ in this case differs appreciably from zero up to $\eta = 0.4$.

In order to further test the accuracy of formula [28], let us assume that

$$F(\eta) = 1-\cos 2\pi\eta.$$

This function will, of course, never be found in any real combustion process but it can serve for a purely mathematical test under very adverse conditions because it differs substantially from zero in the whole interval between 0 and 1. It has a maximum for $\eta = \eta_m = \frac{1}{2}$. Formula [28] then gives the result $V_0 = 2\sqrt{2} = 2.8284$ whereas exact numerical integration gives $V_0 = 2.6782$, i.e., the error is 5.3% only.

In most practical cases of combustion, chemical reactions are confined to temperatures near the upper limit and therefore equation [28] will give very satisfactory results, the error being of the order of about 1%.

Formula [28] bears some resemblance to a formula which was derived by Zeldovitch (18) and by Semenov (16) by neglecting the second and the fourth terms in equation [6] and making other simplifying assumptions. Written in our symbols, the Semenov equation reads

[29] $$V_0 = \left[\frac{2\lambda_f\int_{T_0}^{T_f} U dT}{a_0\rho_0 c_p(T_f-T_0)}\left(\frac{1}{\delta}\right)^{\nu}\left(\frac{N_1}{N_2}\right)^{\nu}\right]^{\frac{1}{2}}.$$

Here a_0 is the initial concentration of fuel, N_1 and N_2 are the total numbers of molecules before and after the over-all reaction, ν is the order of this reaction, δ is an average value of the δ_t, and U is the rate of fuel consumption.

Direct comparison between [28] and [29] is possible if, in the derivation of [28], we disregard the fourth term in equation [6] and consider c_p as constant which is often admissible. Then, substituting from [18a], [19a], [26], [1], and [13], we can write equation [28] in the form

[28a] $$V_0 = \frac{1}{\rho_0 c_p(T_m-T_0)}\left(2\int_{T_0}^{T_f}\lambda Q dT\right)^{\frac{1}{2}}$$

where λQ is a maximum for $T = T_m$.

In the Semenov formula, we can place

$$a_0 = \frac{\rho_0 c_p(T_f-T_0)}{q}$$

where q is the calorific value of the fuel. The correction factors $(1/\delta)^{\nu}$ and $(N_1/N_2)^{\nu}$ can be disregarded for the comparison because in formula [28a] they will be taken care of by the expression to be substituted for Q. Then, if we place $qU = Q$, the Semenov equation appears in the form

[29a] $$V_0 = \frac{1}{\rho_0 c_p(T_f-T_0)}\left(2\int_{T_0}^{T_f}\lambda_f Q dT\right)^{\frac{1}{2}}.$$

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Formula [29a] differs from [28a] in two regards. First, the factor $1/(T_m - T_0)$ is replaced by $1/(T_f - T_0)$. This makes V_0 too small. Second, λ in the integrand is replaced by λ_f. This tends to make V_0 somewhat larger. However, since the integral appears under a square root and since λ is proportional to $\sqrt{T}$, the influence of the factor $1/(T_f - T_0)$ always prevails so that the Semenov formula gives too small values for V_0.

In the more complex cases, e.g., if the δ_i differ very much from each other or if there are indeterminate forms in the expression for Q, the Semenov formula is not applicable.

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ON FLAME PROPAGATION IN EXPLOSIVE MIXTURES OF GASES

II. ON THE DECOMPOSITION FLAME OF OZONE[1]

By Robert Sandri[2]

ABSTRACT

The general theory developed in an earlier paper of the author is applied to the ozone explosion. Values of the linear flame velocity are computed under the assumption of constant enthalpy and, without this assumption, for different values of the reduced diffusion coefficient. The results do not differ very much and are found to be in very good agreement with experiments. They are further compared to the results which were obtained by Hirschfelder *et al.* by exact numerical integration and by Kármán and Penner by an approximation method and are found to be between the values obtained by these authors.

The principal object of the present paper is to test the accuracy and reliability of the general theory of flame propagation developed by the author (7) by applying it to a flame where complete and reliable information concerning kinetic data is available. The explosion flame of mixtures of ozone and oxygen is particularly useful for this purpose. Moreover, it has already served as a sort of "test case" for other theories of flame propagation and thus allows comparison between these and the present theory.

The kinetics of the ozone decomposition has been studied by Wulf (9), Schumacher (8), Kassel (3), and many others. The velocity of the decomposition flame has been measured by Lewis and Elbe (4) by the bomb method. The same authors have developed a theory of flame propagation for this case (5, 6) which is based on the assumptions that the enthalpy is reasonably constant and that an equilibrium is established between atomic oxygen, molecular oxygen, and ozone throughout the flame zone. The first of these assumptions has proved to be correct but the second seems hardly tenable in view of the results of recent research.

Recently, Hirschfelder, Curtiss, and Campbell (1) have applied their theory of flame propagation to the same reaction. Their treatment is virtually free from arbitrary assumptions and their results are in very good agreement with experiments. However, it involves a great many very difficult and complicated numerical computations.

Subsequently, Kármán and Penner (2) solved the problem on the basis of a simplified theory. Their results do not differ much from those of Hirschfelder, Curtiss, and Campbell.

As far as reaction kinetics is concerned, we shall adopt here the same hypotheses as Hirschfelder *et al.* and Kármán and Penner. The over-all reaction is

$$O_3 \rightarrow 1\tfrac{1}{2}O_2 + 34535 \text{ cal.}$$

[1]*Manuscript received October 17, 1955.*
Private contribution.
[2]*Canadian Westinghouse Co. Ltd., Hamilton, Ont. (WT).*

Actually, the following reactions take place:

$$O + O_2 + X \rightleftarrows O_3 + X \pm 24140 \text{ cal.} \quad [I]$$

$$O + O_3 \rightleftarrows 2O_2 \pm 93210 \text{ cal.} \quad [II]$$

$$O_2 + X \rightleftarrows 2O + X \mp 117350 \text{ cal.} \quad [III]$$

where X represents a molecule of any of the components of the mixture.

The rates of these reactions (in mole/sec. cm.^{3}) are given by the formulae

$$[1] \quad U^{(1)} = U_+^{(1)} - U_-^{(1)} = 10^{12} n\sqrt{T}(0.230 n y_1 y_2 - 10.56 y_3 e^{-24140/RT})$$

$$[2] \quad U^{(2)} = U_+^{(2)} - U_-^{(2)} = 10^{12} n\sqrt{T}(7.15 y_1 y_3 e^{-6000/RT} - 2.93 y_2^2 e^{-99210/RT})$$

$$[3] \quad U^{(3)} = U_+^{(3)} - U_-^{(3)} = 10^{12} n\sqrt{T}(8.92 y_2 e^{-117350/RT} - 0.482 n y_1^2)$$

where y_1, y_2, and y_3 are the mole fractions of atomic oxygen, molecular oxygen, and ozone, n is the total concentration (in mole/cm.^{3}), R is the gas constant, and T is the absolute temperature. If we suppose that y_1 is very small throughout the flame zone, it follows from the above formulae that

$$U_-^{(3)} \ll U_+^{(1)}.$$

This term $U_-^{(3)}$ can therefore be disregarded. Likewise it is obvious that $U_+^{(3)}$ and $U_-^{(2)}$ can be neglected because of the large negative exponents. Further, if the concentration of atomic oxygen is very small, its rate of formation or consumption must be near zero so that

$$[4] \quad U^{(1)} + U^{(2)} \approx 0 \approx U_+^{(1)} - U_-^{(1)} + U_+^{(2)}.$$

Consequently

$$[5] \quad y_1 = \frac{10.56 y_3 e^{-24140/RT}}{0.23 n y_2 + 7.15 y_3 e^{-6000/RT}} \approx 1.474 e^{-18140/RT}$$

because the first term in the denominator is found to be very small as compared to the second, except for a negligible range of temperature adjacent to the upper limit T_f where the concentration of ozone is approaching zero so that y_3 becomes comparable to y_1.

The values of y computed by formula [5] are virtually identical to those found by Hirschfelder, Curtiss, and Campbell. They make up only small fractions of a per cent of the mixture so that

$$[6] \quad y_2 + y_3 \approx 1.$$

Equations [5] and [6], together with the hypothesis of constant enthalpy or other assumptions which will be introduced later on, make it possible to compute y_1, y_2, and y_3. Substituting them in the terms for $U_+^{(3)}$, $U_-^{(3)}$, $U_-^{(2)}$, and $U_+^{(1)}$, we can easily verify that these terms are indeed quite negligible.

Thus the system of reactions is virtually reduced to the chain mechanism

$$O_3 + X \rightarrow O_2 + O + X$$

$$O_3 + O \rightarrow 2O_2.$$

In equations [1], [2], and [3], n should read n^2.

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Atomic oxygen is present only as a trace, the concentration of which is determined by the condition that the rate of the above two reactions must be the same, i.e.,

$$U_-^{(1)} = U_+^{(2)}.$$

The concentration y_1 of the atomic oxygen attains a maximum at a temperature less than one degree below T_f. Above that temperature, atomic oxygen is finally consumed, together with the remaining ozone.

It should be emphasized that, although y_1 is very low, it is still far higher than the equilibrium concentration in the whole flame zone except for $T = T_f$, where, of course,

$$U^{(1)} = U^{(2)} = U^{(3)} = 0.$$

This last equation gives extremely low values for both y_{1f} and y_{3f} so that later on we shall place $y_{1f} = y_{3f} = 0$.

Lewis and Elbe (5), on the other hand, assumed that in the entire flame zone

$$U_-^{(1)} = U_+^{(1)}.$$

This could only be true if both $U_-^{(1)}$ and $U_+^{(1)}$ were far larger than $U_+^{(2)}$, which is not consistent with formulae [1] and [2] and leads to values for the flame velocity which are far too high (see Table I).

We can assume with a very good approximation that the specific heat per unit mass of each of the three components is the same. Moreover, no appreciable error is caused by considering c_p as constant. (The same assumptions were made by Hirschfelder *et al.* and by Kármán and Penner.)

In order to apply the general theory (7) we have to find a function $F(\eta)$ which, in this case, is given by the simple formula

$$F(\eta) = \frac{V_0^2\varphi}{T_f - T_0} = \frac{\lambda Q}{\rho_0^2 c_p^2 (T_f - T_0)} \qquad [7]$$

where

$$\eta = \frac{T_f - T}{T_f - T_0}. \qquad [8]$$

Here, λ is the thermal conductivity, Q is the heat produced per unit of time and volume, ρ_0 is the specific mass of the gaseous mixture at the temperature T_0 (the subscript 0 referring to the unburned mixture), V_0 is the linear flame velocity at the same temperature, and c_p is the specific heat per unit mass.

From [I], [II], [1], and [4] we find (disregarding U)

$$Q = -24140\,U_-^{(1)} + 93210\,U_+^{(2)} = 69070\,U_-^{(1)}. \qquad [9]$$

This formula, as we have seen, holds for the entire flame zone except for a very narrow range of temperature near T_f which is not important for the determination of the flame velocity V_0. For c_p an average value is chosen so that the correct flame temperature T_f is obtained:

$$c_p = \frac{y_{30} n_0}{(T_f - T_0)\rho_0} \times 34535 = \frac{y_{30}}{(T_f - T_0) m_0} \times 34535 \qquad [10]$$

In the line above equation [9], U should read $U_+^{(1)}$.

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where m_0 is the molecular weight of the unburned mixture. Moreover, in accordance with Hirschfelder *et al.*, we place

$$\lambda = 5.26 \times 10^{-6}\sqrt{T}.$$

Then, substituting in [7], we find

$$[11] \qquad F(\eta) = 3.23 \times 10^3\left(\frac{T_0}{y_{30}}\right)^2 (T_f - T_0)\frac{e^{-12150/T}}{T} y_3 = K\frac{e^{-A/T}}{T} y_3.$$

We have still to express y_3 as a function of η. To this end we shall first use the hypothesis that the enthalpy is reasonably constant throughout the flame zone. Then, since the concentration of atomic oxygen is negligible, a linear relationship must exist between y_3 and T and consequently

$$[12] \qquad y_3 = y_{30}\eta.$$

The function $F(\eta)$ is found to be virtually zero in the larger part of the interval between 0 and 1 except for small values of η, i.e., near the hot boundary of the flame zone. Under these circumstances the flame velocity can be found with a very good approximation by the formula

$$[13] \qquad V_0 = \frac{1}{1-\eta_m}\left[2\int_0^1 F(\eta)d\eta\right]^{\frac{1}{2}}$$

where $F(\eta)$ is a maximum for $\eta = \eta_m$.

In our case

$$F'(\eta) = \frac{dF}{d\eta} = \left[\frac{1}{\eta} + \frac{T_f - T_0}{T} - \frac{A}{T^2}(T_f - T_0)\right]F(\eta).$$

Placing $F'(\eta_m) = 0$, we find

$$[14] \qquad \eta_m = \frac{T_f^{\,2}}{(A+T_f)(T_f - T_0)}.$$

Further, we find

$$\int_0^1 F(\eta)d\eta = \frac{Ky_{30}}{(T_f - T_0)^2}\{(A+T_f)[-\mathrm{Ei}(-A/T_f) + \mathrm{Ei}(-A/T_0)] - [T_f e^{-A/T_f} - T_0 e^{-A/T_0}]\}$$

$$[15] \qquad \approx \frac{Ky_{30}}{(T_f - T_0)^2}[-(A+T_f)\,\mathrm{Ei}(-A/T_f) - T_f e^{-A/T_f}]$$

where, by definition,

$$-\mathrm{Ei}(-x) = \int_x^\infty \frac{1}{t} e^{-t}dt.$$

Tables for this "exponential integral" are available.

Formulae [13], [14], and [15] make it possible to find V_0. The results are very satisfactory (see Tables I and II). As a matter of fact, Hirschfelder *et al.* (1) found an almost linear relationship between y and T in the entire flame zone, which means that the enthalpy is indeed nearly constant, as supposed.

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However, an even better accuracy can be attained by utilizing the fact that chemical reactions are virtually confined to temperatures near T_f, in order to find a more exact formula for y_3.

According to the general theory (7), the following equations hold:

[16] $$z\left(\frac{dz}{dT}-1\right)+\varphi = 0$$

[17] $$z\frac{d}{dT}\left(\frac{\delta}{m}z\frac{dy_3}{dT}-\frac{y_3}{m}\right)+\psi_3 = 0$$

where

$$z = \frac{\lambda}{V_0\rho_0 c_p}\frac{dT}{dx}$$

[18] $$\delta = \frac{D_{23}\rho c_p}{\lambda}$$

$$\psi_3 = \frac{\lambda U_3}{V_0^2\rho_0^2 c_p}.$$

Here, D_{23} is the diffusion coefficient of the binary mixture of oxygen molecules and ozone, the function φ is defined by equation [7], and U_3 is the rate of production of ozone. Evidently

[19] $$U_3 = U^{(1)}-U^{(2)} = -2U_-^{(1)}.$$

We have now to regard conditions in the neighborhood of T_f. Here the molecular weight of the mixture m is equal to 32. Moreover, λ and all functions of T in equations [1] and [2] can be regarded as constant. The only variable quantities are y_3 and the difference T_f-T or η as defined by [8]. So we have

[20] $$\varphi = \frac{T_f-T_0}{V_0^2}K\frac{e^{-A/T_f}}{T_f}y_3 = \frac{T_f-T_0}{V_0^2}Cy_3.$$

From [7], [9], [10], [18], [19], and [20] we find

[21] $$\psi_3 = -\frac{2c_p}{69070}\varphi = -\frac{y_{30}C}{m_0V_0^2}y_3.$$

Now let

[22] $$y_3 = k\eta$$

[23] $$z = h\eta.$$

Then, substituting in [16], we find

[24] $$h\left(\frac{h}{T_f-T_0}+1\right) = \frac{kC}{V_0^2}(T_f-T_0).$$

Now, it can easily be seen from equations [11], [13], and [22] that the value obtained for V_0 will be proportional to $\sqrt{k}$. With the assumption of constant enthalpy H, the factor of η was y_{30} (see equation [12]). Hence, if we denote by V_{H0} the value of the flame velocity found for H = const., we have

$$\frac{k}{V_0^2} = \frac{y_{30}}{V_{H0}^2}.$$

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Thus we can eliminate k from equation [24] and we find

$$[25] \qquad \frac{h}{T_f - T_0} = -\frac{1}{2} + \sqrt{\left(\frac{1}{4} + \frac{y_{30}C}{V_{H0}^2}\right)}.$$

Substituting from [21], [22], and [23] in [17], we find

$$[26] \qquad V_0^2 = \frac{m}{m_0} \frac{y_{30}C}{[h/(T_f - T_0)]^2\delta + h/(T_f - T_0)}.$$

By means of equations [25] and [26], an improved value V_0 can be computed from V_{H0}. The constant C is defined by equation [20].

The method used here for the improvement of V_0 is similar to the one employed by Kármán and Penner (2), inasmuch as y_3 is assumed to decrease linearly with η in the temperature interval near T_f and as the rate of decrease is determined at the point $\eta = 0$ ($T = T_f$). However, Kármán and Penner do not use equation [13] for the determination of V_0 but a quite different method.

The results obtained by the author of this paper and by other investigators are shown in Tables I and II. Table I shows the values of V_0 obtained for the

TABLE I

FLAME VELOCITY V_0 (CM./SEC.) FOR $y_{30} = 0.25$, $T_0 = 300°$, $T_f = 1250°$

Calculated by Lewis and Elbe	$V_0 = 253$ (for $y_{30} = 0.2466$, $T_f = 1239°$)				
Hirschfelder *et al.*				$V_0 = 51$ for $\delta = 0.75$	$V_0 = 47$ $\delta = 0.94$
Kármán and Penner		$V_0 = 46$ for $\delta = 0.562$	$V_0 = 42$ $\delta = 0.704$		
Author	$V_{H0} = 42.5$	$V_0 = 50.3$ for $\delta = 0.562$	$V_0 = 46.2$ $\delta = 0.704$	$V_0 = 45.0$ $\delta = 0.75$	$V_0 = 41.1$ $\delta = 0.94$

ozone explosion for $y_{30} = 0.25$, $T_0 = 300°$, and $T_f = 1250°$, calculated by Lewis and Elbe (5), by Hirschfelder *et al.* (1), by Kármán and Penner (2), and by the author, for several values of δ. The flame velocity was measured by Lewis and Elbe (4) at 55 cm./sec. for slightly different values of y_{30} and T_f. It will be noted that, for equal values of δ, the results of the author are between those obtained by Kármán and Penner and by Hirschfelder *et al.*

Table II shows the flame velocities measured by Lewis and Elbe for three different ozone explosions and the values calculated for them by Lewis and

TABLE II

FLAME VELOCITY V_0 (CM./SEC.)

y_{30}	T_0	T_f	V_0 meas.	V_0 Lewis and Elbe	V_0 Kármán	V_0 (calc. by author) $\delta = 0.704$	$\delta = 0.94$	V_{H0}
0.2466	300°	1239°	55	253	41	44.5	40	41
0.4005	301°	1680°	141	—	147	151	137	147
0.496	302°	1922°	160	333	225	236	212	231

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Elbe, by Kármán and Penner, and by the author for $\delta = 0.94$ and 0.704 and for $H = \text{const.}$ (The first value of δ is the one generally assumed by Hirschfelder *et al.*, the second, by Kármán and Penner.) The values computed for $\delta = 0.94$ seem to be the best but it will be noted that the assumption of constant enthalpy also gives very satisfactory results.

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ON FLAME PROPAGATION IN EXPLOSIVE MIXTURES OF GASES

III. FLAME PROPAGATION IN MIXTURES OF METHANE AND NITROGEN AIR, HELIUM AIR, AND ARGON AIR[1]

By Robert Sandri[2]

ABSTRACT

The general theory developed in an earlier paper of the author is applied to the combustion of mixtures of methane and nitrogen air, helium air, and argon air where dissociation of the end products is negligible. The oxygen atom chain is assumed to be rate-determining. Absolute values of the flame velocity are computed for mixtures containing 8% of methane and for the stoichiometric mixtures. The results are found to be in very good agreement with experimental values. Dependence on pressure is likewise found to be in very good agreement with experiments. The temperature distribution in the flame zone is also computed.

The combustion of methane has recently been the object of intensive experimental and theoretical research. Measurements of flame velocities in methane–oxygen–nitrogen mixtures by the Bunsen burner method were made by Jahn (5) and by Sachsse and Bartholomé (10). By the same method, Clingman, Brokaw, and Pease (2) carried out measurements on mixtures of methane and nitrogen air, helium air, and argon air. Singer (13) used a careful extrapolation from Bunsen burner measurements to find flame velocities for methane and other hydrocarbons, and Manton, Elbe, and Lewis (7) made measurements by the bomb method.

Bartholomé, Dreyer, and Lesemann (1) calculated the flame velocity in the stoichiometric mixture of methane and air at 200 cm./sec. This value is far too high, chiefly because diffusion was neglected completely in the derivations.

Dugger and Simon (3) used the approximation formulae of Semenov, of Tanford and Pease, and of Manson for calculating relative values of the flame velocity in methane–air mixtures. Of these, the Semenov formula seems to give the best results.

The general theory of flame propagation developed by the author of this paper (11) can easily be applied to the combustion of methane and makes it possible to compute absolute values of the flame velocity which serve as a check for the validity of the assumptions made concerning the mechanism of the reactions involved.

Let us first consider the system of reactions. The over-all reaction is

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 191700 \text{ cal.} \qquad [I]$$

The actual reaction mechanism is, of course, far more complex. Sachsse (9) could explain the results of his experiments on the temperature dependence of the induction time of the methane–oxygen reaction by assuming a reaction

[1]*Manuscript received October 17, 1955.*
Private contribution.
[2]*Canadian Westinghouse Co. Ltd., Hamilton, Ont. (WT).*

mechanism which was first proposed by Norrish (8) and was also assumed by Bartholomé (1):

$$CH_4 + O \rightarrow H_2O + CH_2 \qquad [II]$$

$$CH_2 + O_2 \rightarrow CH_2O + O \rightarrow CO + H_2 + O. \qquad [III]$$

Reaction [II] is supposed to be far slower than [III]. Moreover, carbon monoxide and hydrogen are consumed by subsequent reactions proceeding at a much faster rate than [II], so that reaction [II] is really rate-determining. Since the oxygen atoms are always reproduced in this chain, the concentration of the atomic oxygen is determined by dissociation according to the oxygen equilibrium

$$O_2 \rightleftarrows 2O. \qquad [IV]$$

In view of the high activation energy of [IV], this mechanism holds only for high temperatures near the end temperature T_f where virtually all of the combustion takes place, while in the usual temperature range of kinetic experiments other systems of reactions prevail.

The equilibrium concentration according to [IV] is extremely low even at high temperatures.* Likewise, carbon monoxide and hydrogen are rapidly consumed by other reactions so that only the substances present in the over-all reaction [I] and the nitrogen of the air (or another inert gas replacing it) can exist in appreciable concentration in the gaseous mixture. Under these circumstances, the stoichiometric relations following from [I] must hold throughout the flame zone. Let y_1, y_2, y_3, y_4, and y_5 be the mole fractions of methane, oxygen molecules, carbon dioxide, water, and the inert gas, respectively. Then, since the other mole fractions are negligibly small,

$$[1] \qquad y_1+y_2+y_3+y_4+y_5 \approx 1.$$

Let the subscript 0 refer to the initial mixture of the initial absolute temperature T_0 and the subscript f to the burned flame gas of the temperature T_f. Then

$$[2] \qquad 2(y_{10}-y_1) = y_{20}-y_2 = 2(y_3-y_{30}) = y_4-y_{40}.$$

Since reaction [I] does not change the total number of molecules the mole fraction of the inert gas remains constant:

$$[3] \qquad y_5 = \text{const.} = y_{50}.$$

Equations [2] and [3] make it possible to express all mole fractions by one of them, e.g. y_1, while equation [1] is automatically satisfied.

In order to apply the general theory, it is necessary to express all mole fractions as functions of temperature. This can best be done by using the hypothesis that the enthalpy of the gaseous mixture is reasonably constant throughout the flame zone. This hypothesis has been backed by several authors. It has been found to give very satisfactory results for the ozone

Conditions here differ considerably from those in the ozone explosion (12), because of the absence of a high initial ozone concentration.

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explosion (12) and the very good agreement with experimental results which will be obtained will justify its introduction in the present case.

Therefore, if we disregard the enthalpy of the intermediate products whose concentrations are negligible, we have

$$q(y_{10}-y_1) = C_p(T-T_0). \quad [4]$$

Here, q is the heat produced per mole of methane and C_p is the specific heat per mole of the mixture.

According to the general theory (11), the linear flame velocity V_0 and the temperature distribution in the flame zone can be found by solving the reduced energy equation

$$\zeta\left(\frac{d\zeta}{d\eta}+1\right) = \phi(\eta) \quad [5]$$

with the boundary conditions

$$\zeta = 0 \text{ for } \eta = 0 \text{ and for } \eta = 1.$$

For mixtures which do not contain hydrogen in a high concentration, η and ϕ are given by the formulae

$$\eta = \frac{T_f-T}{T_f-T_0} \quad [6]$$

$$\phi = \frac{\lambda}{(V_0 n_0 C_p)^2}\frac{Q}{T_f-T_0}. \quad [7]$$

Here, λ is the thermal conductivity of the mixture, n_0 is the initial concentration of the mixture (mole/cm.^{3}), and Q is the heat produced per unit of time and volume.

We have now to find Q. Evidently

$$Q = qU_1 \quad [8]$$

where U_1 is the over-all rate of consumption of methane (in mole/sec. cm.^{3}) which can be computed from the number Z of collisions between methane molecules and oxygen atoms. According to the kinetic theory of gases

$$Z = 2N^2 n_1 n_6 \sigma^2 \sqrt{\frac{m_1+m_6}{m_1 m_6} 2\pi RT}. \quad [9]$$

Here, n_1 and n_6 are the concentrations and m_1 and m_6 are the molecular weights of methane and atomic oxygen, N is the number of molecules per mole, and σ is the molecular diameter effective in these collisions.

In order to eliminate n_6, we use the constant of the oxygen equilibrium [III]. According to Bartholomé (1), for the range of temperature under consideration,

$$n_6 \approx \sqrt{(670\, n_2)}\, e^{-58500/RT}. \quad [10]$$

Now let E be the activation energy of reaction [II]. Then

$$U_1 = \frac{Z}{N} e^{-E/RT}. \quad [11]$$

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The function ϕ, as given by equations [7], [8], [9], [10], [11], contains several factors which are always the same and can therefore be replaced once for all by their numerical values:

$$m_1 = m_6 = 16$$

$$R = 8.315 \times 10^7 \text{ ergs/mole degree}$$

$$N = 6.02 \times 10^{23}$$

$$\sigma = 2.6 \times 10^{-8} \text{ cm.}$$

Further, we place

$$\lambda = k\sqrt{T}.$$

The heat conductivity λ is not really proportional to $\sqrt{T}$ but increases faster with temperature. In spite of this, the above assumption is justified because the effective collision diameter σ decreases with increasing temperature so that the product $\lambda\sigma^2$ is very nearly proportional to $\sqrt{T}$.

The activation energy E of reaction [II], according to Harteck and Kopsch (4), is between 3000 and 9500 cal./mole. Sachsse (9) found the activation energy of the over-all process to be equal to 62000 cal./mole. In order to make the sum of the dissociation energy per oxygen atom plus activation energy equal to the experimental value, we place

$$E = 3500 \text{ cal./mole}$$

which is inside the above limits.

Substituting these values and applying the gas law, we find

$$[12] \qquad \phi = 1.557 \times 10^{15} \frac{T_0^2 k}{V_0^2 C_p \sqrt{p}} \frac{y_1\sqrt{y_2}}{y_{10}-y_{1f}} \frac{e^{-31000/T}}{\sqrt{T}}.$$

The pressure p is to be measured in megabars. The mean specific heat C_p varies somewhat with the methane contents of the mixtures and should therefore be computed separately for each mixture.

We have still to express y_1 and y_2 by η. We assume that the end products are not dissociated which is very nearly true if we confine ourselves to the combustion of methane in air or in helium air or argon air because in these cases the end temperature is not excessive.

We have to distinguish three cases: excess of air, stoichiometric mixture, and excess of methane. For an excess of air

$$y_{1f} = 0, \quad y_{2f} = 0.21 - 2.21\, y_{10}$$

and from [2], [4], and [6] we find

$$[13] \qquad \frac{y_1\sqrt{y_2}}{y_{10}-y_{1f}} = \sqrt{2y_{10}}\,\eta\sqrt{\eta+\frac{y_{2f}}{2y_{10}}}.$$

For an excess of methane

$$y_{2f} = 0, \quad y_{1f} = 1.105y_{10} - 0.105, \quad y_{20} = 0.21(1-y_{10}),$$

$$[14] \qquad \frac{y_1\sqrt{y_2}}{y_{10}-y_{1f}} = \sqrt{y_{20}}\left(\eta+\frac{2y_{1f}}{y_{20}}\right)\sqrt{\eta}.$$

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For the stoichiometric mixture

$$y_{1f} = y_{2f} = 0, \quad y_{10} = 0.095,$$

$$[15] \qquad \frac{y_1\sqrt{y_2}}{y_{10}-y_{1f}} = \sqrt{2y_{10}}\,\eta\sqrt{\eta}\,.$$

By substituting these formulae in [12], we obtain ϕ as a function of η, because T is known as a function of η from equation [6].

The flame velocity V_0 is then computed as the eigenvalue of equation [5]. This can be done either by repeated numerical integration or by means of the approximation formula

$$[16] \qquad V_0 = \frac{1}{1-\eta_m}\left[2\int_0^1 F(\eta)d\eta\right]^{\frac{1}{2}}$$

where $F(\eta) = V_0^2\phi$ and ϕ is a maximum for $\eta = \eta_m$. The function $F(\eta)$ does not contain V_0 and is therefore completely known. The integral in [16] can best be evaluated by Simpson's formula.

Numeric calculations according to formula [16] were carried out for 8% methane and 9.5% methane (stoichiometric) in nitrogen air, helium air, and argon air. The results are shown in Table I. The experimental values are those found by Clingman, Brokaw, and Pease (2). The initial temperature was

TABLE I

FLAME VELOCITY V_0 (CM./SEC.)

		V_{exp}	V_{calc}	T_f	$k = \lambda/\sqrt{T}$
N-air	8% CH_4	28	26.5	2036°	3.64×10^{-6}
	9.5% CH_4	39	40.4	2214°	
He-Air	8% CH_4	115	104.1	2408°	11.8×10^{-6}
	9.5% CH_4	132.5	147.8	2514°	
A-Air	8% CH_4	74	73.1	2408°	2.86×10^{-6}
	9.5% CH_4	93.5	103.6	2514°	

chosen as 293°K. and the pressure as one megabar. The mean values of C_p were found by dividing the total heat developed per mole of the mixture by the temperature difference $T_f - T_0$, where T_f was calculated by thermodynamic methods. Thus, allowance was made for the slight amount of actual dissociation of the end products.

The excellent agreement between theory and experiments can be regarded as proof of the correctness of both the mathematical method used and the reaction mechanism and kinetic data assumed.

The present theory is not applicable for a substantial excess of fuel because in this case carbon is primarily formed in the flame zone which results in the presence of carbon monoxide in the burned mixture. The computed flame velocities are consequently too high. Formula [14] can therefore only be used for a very slight excess of methane. In this case the theory predicts an increase of flame velocity beyond the value for the stoichiometric mixture, a result which is well consistent with experience. This is due to the fact that for small

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values of η the function $F(\eta)$ becomes zero of the order $\frac{1}{2}$ while for the stoichiometric mixture it becomes zero of the order 3/2.

Formulae [12] and [16] imply that the flame velocity is proportional to $p^{-0.25}$. Lewis (6), who carried out exact measurements on the pressure dependence of the flame velocity, found for the stoichiometric mixture the pressure exponent $\nu = -0.18$ and for the 8% mixture $\nu = -0.26$. For mixtures containing more methane and oxygen and less nitrogen he found that ν increases and finally becomes positive. This is undoubtedly due to the fact that for these richer mixtures higher end temperatures are attained so that the influence of dissociation becomes considerable at low pressures, thus diminishing the flame velocity at low pressures.

The dependence of V_0 on the initial temperature T_0 and on the specific heat C_p, on the other hand, is not simply expressed by the factor $T_0/\sqrt{C_p}$ because T_0 and C_p also affect the end temperature T_f which in turn greatly affects V_0, so that V_0 increases faster than this factor. The flame velocity should further be proportional to $\sqrt{\lambda}$. The very good results obtained for helium and argon air seem to confirm the correctness of the theory in these regards.

For the stoichiometric mixture of methane and nitrogen air, equation [5] was also solved by repeated numerical integration. This gives an eigenvalue

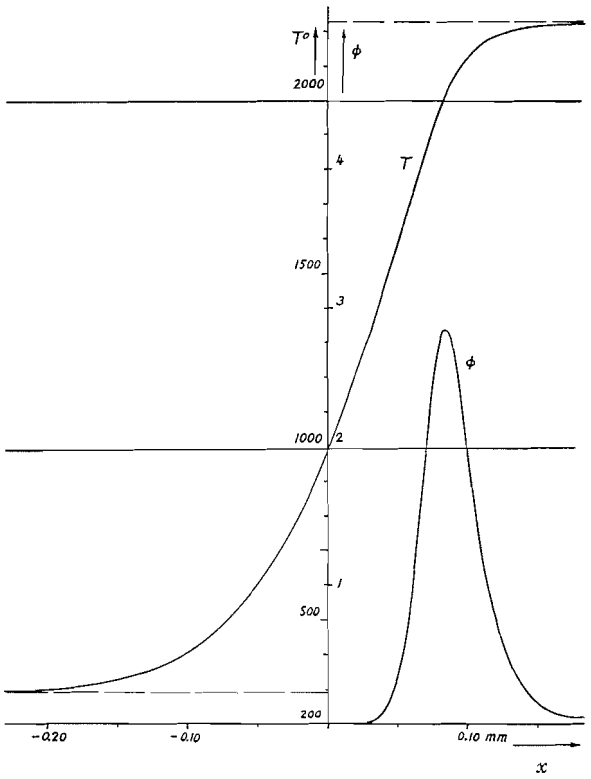

FIG. 1. Temperature and reaction rate in the flame zone.

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$V_0 = 40.8$ cm./sec., as compared to 40.4 obtained by formula [16]. The temperature distribution in the flame zone can then be found by an ordinary quadrature

$$[17] \qquad x = -\frac{1}{V_0 n_0 C_p} \int \frac{\lambda d\eta}{\zeta}.$$

The result is shown in Fig. 1. The integration constant was eliminated by placing $x = 0$ for $T = 1000°$. The temperature limits T_0 and T_f are attained only for $x = \mp \infty$. However, the thickness of the flame zone is practically very small (0.2 mm. for 95% of the total temperature difference), a result which is very well consistent with generally adopted ideas about the structure of flame zones.

The same figure shows also the quantity ϕ which is proportional to the rate of reaction [II] as well as to the rate of heat development, plotted against x. Most of the heat development takes place at temperatures near T_f.

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THE ALDOBIOURONIC ACIDS OF HEMICELLULOSE B OF OAT HULLS[1]

By E. L. Falconer[2] and G. A. Adams

ABSTRACT

Partial hydrolysis of hemicellulose B from oat hulls yielded two aldobiouronic acids, which were identified as 2-*O*-(4-*O*-methyl-α-D-glucopyruronosyl)-D-xylose and 2-*O*-(α-D-glucopyruronosyl)-D-xylose respectively. In addition, two aldotriouronic acids were isolated, one yielding on hydrolysis xylose and 4-*O*-methylglucuronic acid, and the other, xylose, galactose, and glucurone.

INTRODUCTION

Previous investigations (2, 5, 8) have shown that the extractable hemicelluloses of oat hulls consist principally of xylan, with which small amounts of araban are either combined or admixed. Acid hydrolysis of the hemicelluloses also released uronic acids among which an aldotriouronic acid, containing D-galactose and D-glucuronic acid, was reported (2). This acid has never been reported as a component of other cell wall polysaccharides although similar acids have been isolated from plant gums. Since the previous investigations were carried out before the modern techniques of chromatography became available, it was felt that a further examination of the acid components of oat hull hemicellulose would be of interest.

In the present study the hemicelluloses of extractive-free, pectin-free oat hulls were isolated by successive extractions with 2% sodium carbonate, 5% sodium hydroxide, and 10% sodium hydroxide. These fractions were in turn separated into hemicellulose A, which was precipitated on slight acidification of the extracts with acetic acid, and into hemicellulose B, which remained soluble in the acidified extract but was precipitated with four volumes of ethanol. All hemicellulose fractions isolated by the various extraction procedures were composed primarily of D-xylose and L-arabinose residues. Two fractions (5B and 10A, Table I) also contained small amounts of D-galactose and D-glucose respectively. The fractions extracted with sodium carbonate (2A and 2B) had a high uronic acid content. A similar observation was made by Mitchell and Ritter (9) on the fraction of maple wood holocellulose soluble in 2% sodium carbonate. Since the uronic acids of fractions 5A and 5B showed similar compositions, the acidic oligosaccharides of fraction 5B, the largest hemicellulose fraction, were selected for further study.

The acidic components formed by partial hydrolysis of hemicellulose 5B were isolated by ion exchange resin and were separated by paper chromatography into four fractions. The relative proportion and analysis of the four fractions are shown in Table II. By equivalent weight estimations fractions I and III were shown to be aldotriouronic acids with fraction I containing

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galactose, xylose, and glucurone and fraction III being composed of xylose and 4-*O*-methyl glucuronic acid. Fractions II and IV were aldobiouronic acids composed of glucuronic acid → xylose and 4-*O*-methyl glucuronic acid → xylose respectively. Reduction of these uronic acid fractions yielded the corresponding disaccharides after which the monosaccharide components were identified by hydrolysis and isolation of suitable crystalline derivatives.

Methylation and hydrolysis of the disaccharides obtained by reduction of fractions II and IV provided a means of locating the glycosidic bond attachments. An improved method of methylation was employed using dimethyl sulphate with solid sodium hydroxide in anhydrous tetrahydrofuran instead of water. Only one methylation treatment with these reagents was required to convert the methyl glucosyl-xyloside to a fully methylated product. Since the resulting methylated sugars from each fraction were chromatographically identified in three solvents and found to be identical only those from fraction IV were fully characterized as 2,3,4,6-tetra-*O*-methyl-D-glucopyranose and 3,4-di-*O*-methyl-D-xylose by physical constants and derivative formation. The results showed that fraction II was 2-*O*-(α-D-glucopyruronosyl)-D-xylose and that fraction IV was analogous to it but containing a methyl ether at C(4) of the glucuronic acid. Fraction IV was, therefore, identical with the aldobiouronic acid isolated from hemicelluloses of aspen wood (7), corn cobs (10), beechwood (3), scots pine, and black spruce (4). Fraction II was the same as the aldobiouronic acid obtained from sapote gum (12). Aldobiouronic acids identical with fractions II and IV have been found together previously only in hydrolyzates of wheat bran (1) and corn cob hemicelluloses respectively (10, 11).

The presence of galactose as part of the aldobiouronic acid (fraction I, hemicellulose 5B) could not be established because sufficient quantities of material were not available for a structural study. However, it seems clear that the main uronic acid component from oat hulls contains xylose and not galactose as its neutral sugar component. The results of the present investigation show that the main uronic acid components of oat hull hemicelluloses fit the general pattern of the glucuronic acid – xylose acids found in the cell wall hemicellulose of many plants.

EXPERIMENTAL

Paper Chromatography

Separations were performed by the descending technique on Whatman No. 1 filter paper. A saturated aqueous-butanol solution of aniline hydrogen oxalate was used as the spray reagent. The following solvents (v/v) were used: (A) ethyl acetate – acetic acid – formic acid – water (18: 3: 1: 4), (B) ethyl acetate – pyridine – water (2: 1: 2; upper layer), (C) 2-butanone–ethanol–water (20: 5: 2), and (D) benzene–ethanol–water (169: 47: 15; upper layer).

Preparation of Oat Hull Hemicelluloses

Finely-ground oat hulls were extracted with the benzene–ethanol azeotrope (2: 1) for two days in a Soxhlet apparatus. After being air-dried, the material was extracted for three hours with 0.5% ammonium oxalate at 80–85°C.

and for 16 hr. with the same extractant at room temperature, and was finally washed by stirring with large quantities of water at room temperature. The extractive-free, depectinized hulls were then consecutively and exhaustively extracted at room temperature with 2% sodium carbonate, 5% sodium hydroxide, and 10% sodium hydroxide; the alkali extractions being carried out in a nitrogen atmosphere. Acidification of the filtered extracts with glacial acetic acid yielded precipitates of hemicelluloses A, and concentration of the filtrates and precipitation into four volumes of ethanol yielded hemicelluloses B. The hemicelluloses were recovered by centrifuging, washed with 80% (v/v) aqueous ethanol, slurried with water, and dialyzed against distilled water. The resulting slurries were poured into four volumes of vigorously stirred ethanol, washed with ethanol, rinsed with ether, and dried *in vacuo*. Yields, based on the oven-dried, extractive-free oat hulls, and ash (sulphated) contents are given in Table I.

TABLE I

YIELDS AND ASH CONTENTS OF CRUDE HEMICELLULOSES FROM DRIED, EXTRACTIVE-FREE OAT HULLS

Extractant	Hemicellulose fraction	Yield, %	Sulphated ash, %
2% sodium carbonate	2A	0.10	38.01
	2B	0.40	28.53
5% sodium hydroxide	5A	12.3	4.78
	5B	14.9	12.00
10% sodium hydroxide	10A	0.49	2.21
	10B	1.86	8.91

Qualitative Examination of Hemicellulose Fractions for Sugar Components

The hemicellulose fractions were all light brown powders which were partially soluble in water. Hydrolysis with 3% sulphuric acid for 12 hr. and paper chromatographic examination of the hydrolyzates using solvent B showed xylose and arabinose to be the principal constituents of all fractions. Galactose occurred only in fraction 5B and glucose in fraction 10A. Fractions 2A and 2B had relatively high uronic acid contents. No other differences between the fractions were evident. The residue which remained after the alkaline extractions yielded glucose, xylose, and arabinose on hydrolysis. Insoluble lignin-like material remaining after acid hydrolysis amounted to 7.84% for fraction 5A and to 18.38% for fraction 5B. Isolation by means of an anion exchange resin (Amberlite IR-4B), and further paper chromatographic examination of the acid constituents of the hydrolyzates of fractions 5A and 5B using solvent A revealed that these fractions had similar compositions. Further study was therefore concentrated on fraction 5B where these components occurred in apparently larger amounts.

Separation of the Uronic Acid Constituents of Hemicellulose Fraction 5B and Identification of the Sugar Components

Hemicellulose 5B (75 gm.) was partially dissolved by stirring in hot water (2 liters) for one hour. A 4% solution of sulphuric acid (1850 ml.) was then added and the mixture was boiled under reflux for 11 hr. The insoluble material

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was separated by centrifuging and again heated for an additional 10 hr. in 3% sulphuric acid (1 liter). The acid hydrolyzate was heated to about 80°C., brought to pH 5.6 by solid barium hydroxide and then to neutrality with barium carbonate. Decolorizing charcoal was stirred into the hot mixture, and after settling and cooling, the clear supernatant liquid was poured off and filtered. The filtrate was passed slowly through a double column containing Amberlite IR-120 cation-exchange resin (150 ml.) followed by an equal volume of IR-4B anion-exchange resin, and the resins were washed with large quantities of water until the washings were negative to the anthrone test (6). The column was dismantled, and the IR-4B resin containing the absorbed uronic acids was transferred to a beaker. The resin was stirred in 4% sulphuric acid (1060 ml.) for one hour after which the uronic acids were recovered by washing the resin, in a column, with 0.02 *N* sulphuric acid. The eluate was neutralized with barium carbonate, filtered, and finally passed through IR-120 cation-exchange resin (150 ml.) before being concentrated to a sirup (4 gm.). A paper chromatogram of the sirup developed in solvent A showed four components with R_x (rate of flow relative to xylose) values of 0.09, 0.27, 0.36, and 0.68 together with small amounts of D-xylose and a methoxyglucuronic acid, R_x 1.45.

A sample of the sirup containing the mixed uronic acids was converted to the methyl glycoside methyl ester mixture and reduced with lithium aluminum hydride in tetrahydrofuran (as described later). Hydrolysis of the reduced oligosaccharides and paper chromatographic examination using solvents B and C indicated the presence of D-glucose, D-xylose, and 4-*O*-methyl-D-glucose. Separation of the sugar mixture on large sheets of paper was carried out in solvent C for 17 hr. at 28°C. Recovery of the three materials yielded:

(*a*) Four parts (by weight) of a sirup corresponding to α-D-glucopyranose: $[\alpha]_D^{25}$ +44.1° (*c*, 3.6 in water); osazone, dec. 202–204°C. An X-ray powder pattern of the osazone confirmed its identity with that of an authentic sample of D-glucosazone.

(*b*) Nine parts of crystalline α-D-xylopyranose: $[\alpha]_D^{25}$ +56.6° (7 min.)→+19° (1.5 hr., constant) (*c*, 2.5 in water), m.p. and mixed m.p. 144–145.5°C. (from ethanol). The X-ray powder pattern of these crystals was identical with that of a known sample.

(*c*) Seven parts of a sirup of 4-*O*-methyl-D-glucopyranose: $[\alpha]_D^{25}$ +57.2 (*c*, 1.6 in water); osazone, $[\alpha]_D^{25}$ −32 (10 min.) → +9 (48 hr., constant) (*c*, 0.5 in 2% ethanolic pyridine); m.p. and mixed m.p. 158.5–159.5°C. (from benzene containing a little ethanol). The identity of the osazone was confirmed by comparison of its X-ray powder pattern with that of a known sample of 4-*O*-methyl-D-glucosazone.

These observations confirm the presence of D-xylose, D-glucuronic acid, and 4-*O*-methyl-D-glucuronic acid as the principal monosaccharide components of the acid fraction of hemicellulose 5B.

Chromatographic Separation of Uronic Acid Fraction Components from a Hydrolyzate of Hemicellulose 5B

The uronic acids from a partial hydrolysis of the hemicellulose were separated on 30 sheets of Whatman No. 1 filter paper (11.25 in. × 18.5 in.) using solvent

A and a developing time of 25 hr. The various fractions were eluted from the paper with water, the solutions were concentrated to small volume, decolorized with charcoal, and evaporated to dryness. Properties of these fractions are shown in Table II.

TABLE II

PROPERTIES OF THE URONIC ACID FRACTIONS FROM HEMICELLULOSE B OF OAT HULLS

Fraction	Weight ratio	R_x* (solvent A)	$[\alpha]_D^{25}$	Neutn. equiv.	OMe, %	Sugar components†
I	1	0.09	+40	440	1.42	Galactose, xylose, glucuronic acid
II	5	0.27	+88.4	332	1.00	Xylose, glucuronic acid
III	2	0.36	+79	440	6.76	Xylose, 4-*O*-methyl glucuronic acid
IV	6.5	0.68	+94.5	346	8.54	Xylose, 4-*O*-methyl glucuronic acid

*R_x = *rate of flow relative to* D-*xylose.*
†*Based on chromatographic identifications.*

Examination of Uronic Fraction IV

The material had a higher R_x value (0.68) than galacturonic acid (R_x 0.50) in solvent A in which glucuronic acid moved completely as glucurone (R_x 1.80). This observation was further evidence suggesting the presence of a methoxyl group. Anal.: Calc. for $C_{11}H_{17}O_{10}(OCH_3)$: OMe, 9.12%; equiv. wt. 340.3. Found: OMe, 8.54%; equiv. wt., 346.

Hydrolysis of the aldobiouronic acid with *N* sulphuric acid for 16 hr. in a sealed tube at 110°C. followed by paper chromatography with solvents A and B revealed the presence of D-xylose and 4-*O*-methyl-D-glucuronic acid in addition to some unchanged material.

A sample of the aldobiouronic acid (527 mgm.) was converted to the glycoside, ester form by heating with 2% methanolic hydrogen chloride (25 ml.) for six hours under reflux. The methyl glycoside methyl ester of the aldobiouronic acid (524 mgm.) in tetrahydrofuran (50 ml.) was reduced by dropwise addition of a solution of lithium aluminum hydride (600 mgm.) in tetrahydrofuran (25 ml.). The product (497 mgm.) was hydrolyzed by heating at 100°C. for six hours with *N* sulphuric acid and chromatographic examination (solvents B and C) of the hydrolyzate showed the presence of xylose and 4-*O*-methyl glucose.

Methylation of the Disaccharide

The 4-*O*-methyl-D-glucosyl-D-xylose (497 mgm.) in water (3 ml.) was methylated by dimethyl sulphate (1.5 ml.) and 30% sodium hydroxide (3.0 ml.). Three additions of reagents were made before the mixture was brought to pH 8.9 by sulphuric acid and the product was recovered by continuous extraction with chloroform. Evaporation of the chloroform extract yielded a sirup (463 mgm.) which exhibited a small infrared absorption maximum at 3480 $cm.^{-1}$ indicating the presence of free hydroxyl groups.

Complete methylation of the sirup (448 mgm.) was obtained by the dropwise addition over three hours of dimethyl sulphate (3 ml.) to a stirred solution

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of the sirup in pure tetrahydrofuran (15 ml.) containing pulverized sodium hydroxide (2.6 gm.). The reaction was carried out for 16 hr. in a flask partially immersed in a water bath at 23–28°C., after which enough water was added to bring the solids into solution. The temperature of the water bath was raised to 60°C., the tetrahydrofuran was evaporated by a stream of nitrogen, and the temperature was maintained for an hour to ensure the complete decomposition of the dimethyl sulphate. The mixture was cooled, partially neutralized to pH 8.9 with sulphuric acid, and extracted with chloroform. Evaporation of the chloroform extract yielded a sirup which was freed from impurities by filtration of its methanol solution. Evaporation of the methanol and drying of the resultant sirup afforded a product (400 mgm.), $[\alpha]_D^{25}$ +114° (*c*, 1.4 in chloroform) whose infrared spectrum indicated only a slight trace of hydroxyl groups. Anal.: Calc. for $C_{11}H_{13}O_3(OCH_3)_7$: OMe, 52.92%. Found: OMe, 51.7%.

Hydrolysis of the Methylated Disaccharide and Separation of the Products

The methylated disaccharide (366 mgm.) was heated under reflux with 4% methanolic hydrogen chloride (25 ml.) for 15 hr., and after evaporation of the acid under reduced pressure, with boiling *N* hydrochloric acid (25 ml.) for six hours. The hydrolyzate was deionized by Amberlite resins IR-120 and IR-4B and the resulting solutions were evaporated to a sirup (221 mgm.). Paper chromatography of this sirup in solvents C and D indicated the presence of two components giving the same color reactions with the spray reagent and moving concurrently with 3,4-di-*O*-methyl-D-xylose and 2,3,4,6-tetra-*O*-methyl-D-glucose. The sugars were separated on large sheets of paper in solvent D (4.5 hr.). The individual sugars were recovered by removal and elution of the appropriate zones with water, treatment of the concentrated solutions with activated charcoal and with mixed resins (IR-120 and IR-4B) followed by evaporation to sirups. Filtration of the materials from ethyl acetate solutions and evaporation of the solvent yielded pure sirups of dimethylxylose (58.8 mgm.) and tetramethylglucose (86.3 mgm.). The tetramethylglucose sirup crystallized spontaneously on standing.

Identification of 3,4-Di-O-methyl-D-xylose

The dimethylxylose was a colorless sirup, $[\alpha]_D^{25}$ +19° (*c*, 1.6 in water), producing brick-red spots of R_g 0.38 on paper chromatograms developed with solvent D and sprayed with the aniline hydrogen oxalate reagent. The methylated sugars, 2,4-di-*O*-methyl-D-xylose, 2,3-di-*O*-methyl-D-xylose, and 2,3,4-tri-*O*-methyl-D-xylose, gave dark brown spots of R_g values 0.27, 0.31, and 0.89 respectively on similarly prepared chromatograms.

The 3,4-di-*O*-methyl-D-xylose (37.8 mgm.) in water (1 ml.) was oxidized with bromine (0.025 ml.) for 42 hr. at room temperature. The product (24.9 mgm.) crystallized after nucleation with 3,4-di-*O*-methyl-D-xylonolactone. Recrystallization from ether containing a small amount of *n*-hexane yielded colorless needles, $[\alpha]_D^{25}$ −48 (15 min.) → −20 (54 hr., constant) (*c*, 1.0 in water); m.p. and mixed m.p. 67–68°C. The dimethylxylose was therefore 3,4,-di-*O*-methyl-D-xylopyranose.

Identification of 2,3,4,6-Tetra-O-methyl-D-glucose

Recrystallization of the tetramethylglucose from ether – petroleum ether afforded light yellow needles, $[\alpha]_D^{25}$ +88.1 (15 min.) → +83.2 (4.5 hr., constant) (*c*, 1.4 in water); m.p. and mixed m.p. 83.0–95.5°C.

The 2,3,4,6-tetra-*O*-methyl-D-glucopyranose (60 mgm.) was converted to the anilide (7). Recrystallization several times from *n*-hexane and from ethanol yielded colorless needles of 2,3,4,6-tetra-*O*-methyl-*N*-phenyl-D-glucosylamine, m.p. 116–117°C.; $[\alpha]_D^{25}$ +205 (*c*, 1.2 in acetone).

Characterization of Uronic Fraction II

A sample of fraction II was placed in a sealed tube with *N* sulphuric acid for 16 hr. at 110°C. Paper chromatography of the hydrolyzate in solvents A and B indicated the presence of D-xylose and D-glucurone. Treatment of the aldobiouronic acid with 2% methanolic hydrogen chloride produced the methyl glycoside methyl ester which was reduced with lithium aluminum hydride in tetrahydrofuran to the methyl glycoside of the corresponding disaccharide. Acid hydrolysis of this disaccharide liberated D-xylose and D-glucose as shown by examination of paper chromatograms developed in solvent B.

Complete methylation of the glucosyl-xylose methyl glycoside was accomplished by the same method as described for fraction IV and yielded a sirup (108 mgm.), $[\alpha]_D^{25}$ +110 (*c*, 1.1 in chloroform) whose infrared spectrum indicated the total absence of hydroxyl groups. Anal.: Calc. for $C_{11}H_{13}O_3(OCH_3)_7$: OCH_3, 52.92%. Found: OCH_3, 52.5%.

A solution of the hepta-*O*-methyl-glucosyl-xylose in 4% methanolic hydrogen chloride was heated in a sealed tube for 15 hr. at 80°C. Subsequent hydrolysis with aqueous *N* hydrochloric acid followed by chromatographic examination in solvents B, C, and D revealed the presence of two methylated reducing sugars moving adjacently to and producing the same color reactions with the spray reagent as did 3,4-di-*O*-methyl-D-xylose and 2,3,4,6-tetra-*O*-methyl-D-glucose.

Since these components were the same as those previously identified from fraction IV no further characterization was done.

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FREE RADICALS BY MASS SPECTROMETRY

X. THE IONIZATION POTENTIALS OF METHYL SUBSTITUTED ALLYL RADICALS[1]

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ABSTRACT

The vertical ionization potentials of the β- and γ-methyl substituted allyl radicals as measured by electron impact are 8.03±0.05 v. and 7.71±0.05 v., respectively. From appearance potential data the following bond dissociation energies can be derived, assuming the dissociation processes to be free from complications:

$$D(CH_2{:}\,C(CH_3)CH_2{-}I) = 31.6{\pm}2 \text{ kcal./mole}$$
$$D(CH_3CH{:}\,CHCH_2{-}I) = 33.2{\pm}2 \text{ kcal./mole.}$$

With assumptions about the structure of the ions produced by electron impact from the corresponding butenes the dissociation energies of the C_4H_7—H bonds in these latter compounds can be estimated, and the heats of formation of the corresponding radicals derived, namely:

$$\Delta H_f^\circ(CH_2{:}\,C(CH_3)\dot{C}H_2) = 21{\pm}3 \text{ kcal./mole}$$
$$\Delta H_f^\circ(CH_3CH{:}\,CH\dot{C}H_2) = 26{\pm}3 \text{ kcal./mole.}$$

From data on the allyl halides we evaluate the heat of formation of the allyl radical to be:

$$\Delta H_f^\circ(CH_2{:}\,CH\dot{C}H_2) = 32{\pm}6 \text{ kcal./mole.}$$

INTRODUCTION

Of the eight structures possible for C_4H_7 radicals three can be regarded as methyl substituted allyl radicals and consequently should have a delocalization energy of about the same order as that attributed to the allyl radical itself. These three radicals are:

$$CH_3\dot{C}HCH{:}\,CH_2 \quad (\alpha)$$
$$CH_3CH{:}\,CH\dot{C}H_2 \quad (\gamma)$$
$$CH_2{:}\,C(CH_3)\dot{C}H_2 \quad (\beta)$$

As derivatives of the allyl radical by methyl substitution these can be called the α-, γ-, and β-methallyl radicals respectively. The first two structures are interconvertible by electron migration without a proton shift, and according to this view these radicals may be regarded as resonance hybrids with an intermediate structure rather than as separate entities.

It was thought to be of interest to attempt the preparation of the three methallyl radicals by pyrolysis of the corresponding iodides to see if the ionization potentials of the radicals produced from the α- and γ-methallyl iodides were in fact identical. It would also be of interest to determine the effect on the ionization potential of the allyl radical of substitution of methyl in these positions.

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The β-methallyl radical has been suggested as an intermediate in the pyrolysis of isobutene (17, 16) and as a product of the primary dissociation in the same pyrolysis (23). From kinetic considerations it was concluded that the thermal dissociation of the radical led to the formation of allene and a methyl radical

$$CH_2{:}\,C(CH_3)\dot{C}H_2 \rightarrow CH_2{:}\,C{:}\,CH_2 + \dot{C}H_3. \qquad [1]$$

The γ-methallyl or crotyl radical does not seem to have been studied very much. The pyrolysis of 2-butene, in which its formation seems likely, has not been investigated as thoroughly as that of 1-butene. The pyrolysis of the latter compound has been shown to yield a methyl and an allyl radical (19, 9) instead of forming the α-methallyl radical by loss of a hydrogen atom. The equivalent process for 2-butene, namely

$$CH_3CH{:}\,CHCH_3 \rightarrow CH_3CH{:}\,\dot{C}H + \dot{C}H_3, \qquad [2]$$

would seem to be improbable since, without isomerization, the structure of this radical does not allow a delocalization energy of the order available to the allyl radical. The activation energy for the decomposition of 2-butene, based on preliminary work, was found by Molera and Stubbs (14) to be 57.4 kcal./mole as compared to 66.4 kcal./mole for 1-butene. This difference does not seem to be a measure of the dissociation energies of the bonds broken in the two primary processes, for the primary split for 2-butene is, probably,

$$CH_3CH{:}\,CHCH_3 \rightarrow CH_3CH{:}\,CH\dot{C}H_2 + H \qquad [3]$$

and, of course, the dissociation energy for the R—H bond in equation [3] is almost certainly greater than that of the allyl—CH_3 bond in 1-butene.

PREPARATION OF METHALLYL IODIDES

(*a*) *β-Methallyl Iodide* (*CH_2: $C(CH_3)CH_2I$*)

Commercial methallyl chloride was purified by distillation in a 100 cm. column packed with glass helices. In a second distillation a fraction having a boiling point of 71.9° C. at 756 mm. was collected. This fraction was refluxed for one hour with an excess of a saturated solution of sodium iodide in acetone. After the addition of water, the methallyl iodide was separated and washed with successive portions of water. It was then dried and distilled twice at reduced pressure, the middle fraction being retained. The mass spectrum showed that a trace of the dimer of the β-methallyl radical, 2,5-dimethyl 1,5-hexadiene, was present, but no other impurities were detected.

(*b*) *γ-Methallyl Iodide* (*CH_3CH: $CHCH_2I$*)

This was prepared (24) by passing butadiene through 57% aqueous HI at 20° C. The product was separated and purified by several bulb-to-bulb distillations. The infrared spectrum showed that this sample was the γ-isomer. The refractive index at 23° C. was 1.5500.

(*c*) *α-Methallyl Iodide* (*CH_3CHICH: CH_2*)

All attempts to produce this isomer resulted instead in the production of the γ-isomer. α-Methallyl bromide was prepared by the addition of butadiene to anhydrous HBr under antioxidant conditions (8). After being freed from

HBr and butadiene by bulb-to-bulb distillation, the product had a refractive index at 23° C. of 1.4617, in good agreement with $\eta_{23} = 1.4608$ given by Kharasch *et al.* The infrared spectrum showed that this product was the α-isomer, essentially free from γ-methallyl isomer even after several days' storage at 0° C. However when the bromide was treated with NaI in acetone the resulting methallyl iodide after low-pressure distillation was found by infrared analysis to have almost completely rearranged to the γ-isomer.

It was thought that the isomerization might have occurred during the low-pressure distillation. An attempt was therefore made to prepare the α-methallyl iodide directly from butadiene and anhydrous HI in a manner analogous to the preparation of the bromide. Anhydrous HI was prepared (1) by the reaction of iodine vapor and hydrogen on platinized asbestos. This was condensed into a trap containing butadiene and a little diphenylamine cooled in liquid nitrogen. The liquid nitrogen was then replaced by a dry-ice acetone mixture. As soon as the contents of the trap liquified, reaction occurred, as indicated by a sharp but temporary increase in pressure. The resulting methallyl iodide was freed from butadiene and HI by bulb-to-bulb distillation. The infrared spectrum showed, however, that this product was essentially pure γ-methallyl iodide. In view of the ease of isomerization of α-methallyl bromide (8) it is probable that the isomerization

$$CH_3CHICH{:}CH_2 \rightarrow CH_3CH{:}CHCH_2I \qquad [4]$$

is very rapid even at low temperatures.

PRODUCTION OF THE RADICALS

The methallyl radicals were produced by pyrolysis of the corresponding iodides in a low pressure reactor attached to the ion source of a mass spectrometer, the reactor being the same as that used earlier to produce the ethyl, isopropyl, and propargyl radicals (4). The modified mass spectrometer and its operation have been described (12, 11).

(*a*) *β-Methallyl Radicals*

At a reactor temperature of 825° C., the β-methallyl iodide was almost completely decomposed as indicated by the parent peak at mass 182. Using electrons of low energy, observations of the mass 55 peak showed methallyl radicals to be present in abundance. With electrons of 50 v. energy the dimerization product 2,5-dimethyl 1,5-hexadiene was also found to be present. From a pure sample, the ratio of peaks 55/95 in the mass spectrum of the latter was measured. Using this ratio and the ratio of peaks 55/182 in the spectrum of β-methallyl iodide, the net peak height at mass 55 attributable to methallyl radicals could be measured. A net peak of 8×10^{-12} amperes for the radical could be obtained without difficulty. With higher temperatures up to 1050° C., the amount of β-methallyl radicals decreased, the decomposition products being methyl radicals and allene as found by Szwarc (23).

(*b*) *γ-Methallyl Radicals*

The behavior of γ-methallyl iodide was essentially the same as that of the β-isomer, the iodide being almost completely decomposed at 825° C. Methallyl

radicals and a dimer, presumably 2,6-octadiene, were produced. The ratio 55/95 in the spectrum of 2,6-octadiene was obtained from a sample prepared by heating γ-methallyl iodide in contact with zinc dust, followed by vacuum distillation. With reactor temperatures up to 1050° C. the amount of methallyl radicals decreased, the products in this case being butadiene and hydrogen:

$$CH_3CH{:}\,C\dot{H}CH_2 \rightarrow CH_2{:}\,CHCH{:}\,CH_2 + H. \qquad [5]$$

It was not established whether the butadiene was the 1,2- or the 1,3-isomer. A net peak of 4×10^{-12} amperes for the radical could be easily produced.

MEASUREMENT OF THE IONIZATION POTENTIALS

Using 50 v. electrons, the net peak heights at mass 55 for the radicals were obtained by subtracting the contributions from the dimers and from the undecomposed fraction of methallyl iodides as described above. The method of measurement of the ionization potentials of the radicals was the same as that described previously (9). Ionization efficiency curves for the radical ion and for the krypton 84 ion were measured alternately. The voltage difference (δV) between these curves was plotted against the peak height (I) and the resulting curve was extrapolated to $I = 0$ (25, 13). For comparison the voltage difference of the β-methallyl radical ion was also determined by the "vanishing-current" method (20, 21). The appearance potentials for the β- and γ-methallyl ions from the iodides were also measured.

RESULTS AND DISCUSSION

(*a*) *Ionization Potentials*

In Table I are given the values found for the vertical ionization potentials of the methallyl radicals by the method of extrapolated voltage differences,

TABLE I

IONIZATION POTENTIAL OF β- and γ-METHALLYL

Radical	Ionization potential (volts)	
	Individual values	Average
$CH_2{:}\,C(CH_3)\dot{C}H_2$ (β)	8.03 8.03 8.02	8.03±0.05
"Vanishing-current" method	8.01	
$CH_3CH{:}\,C\dot{H}CH_2$ (γ)	7.72 7.73 7.68	7.71±0.05

each being the average of three determinations. The limits of error were estimated from the uncertainty in the extrapolation of the δV vs. I curves, the ones for the β-methallyl radical being shown in Fig. 2. Fig. 1 shows the ionization efficiency curves for krypton 84 and the β-methallyl radical, from which the "vanishing-current" method yields a value of $I(\beta\text{-methallyl}) = 8.01$ v., in good agreement with the values determined by the other method.

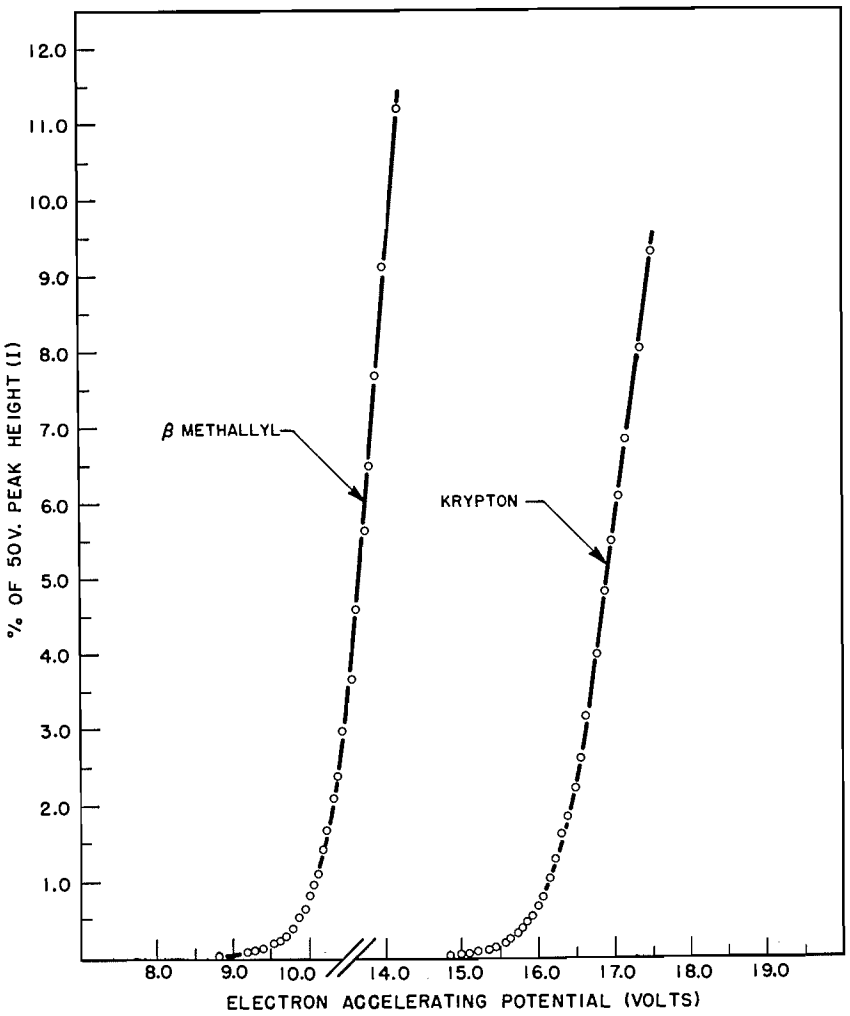

FIG. 1.

The conclusion that the difference in the ionization potentials of the β- and γ-methallyl radicals does not result from an error in the calibration of the voltage scale received confirmatory evidence from a preliminary experiment in which a sample of methallyl iodide prepared from commercial β-methallyl chloride was pyrolyzed. The ionization efficiency curve for mass 55 had a sigmoid shape at low electron energy, indicating the presence of two radical species of the same mass but with different ionization potentials. Using methallyl iodide prepared from a redistilled sample of the commercial β-methallyl chloride, the sigmoid shape was completely absent.

It is interesting to compare these ionization potentials with the 8.16 ± 0.03 v. obtained for the allyl radical (9). The substitution of a methyl group for the β-hydrogen in allyl causes a decrease of only 0.13 ± 0.08 v., while the substitution of a γ-hydrogen causes a decrease of 0.45 ± 0.08 v. Although there is some disagreement about the ionization potentials of the corresponding hydro-

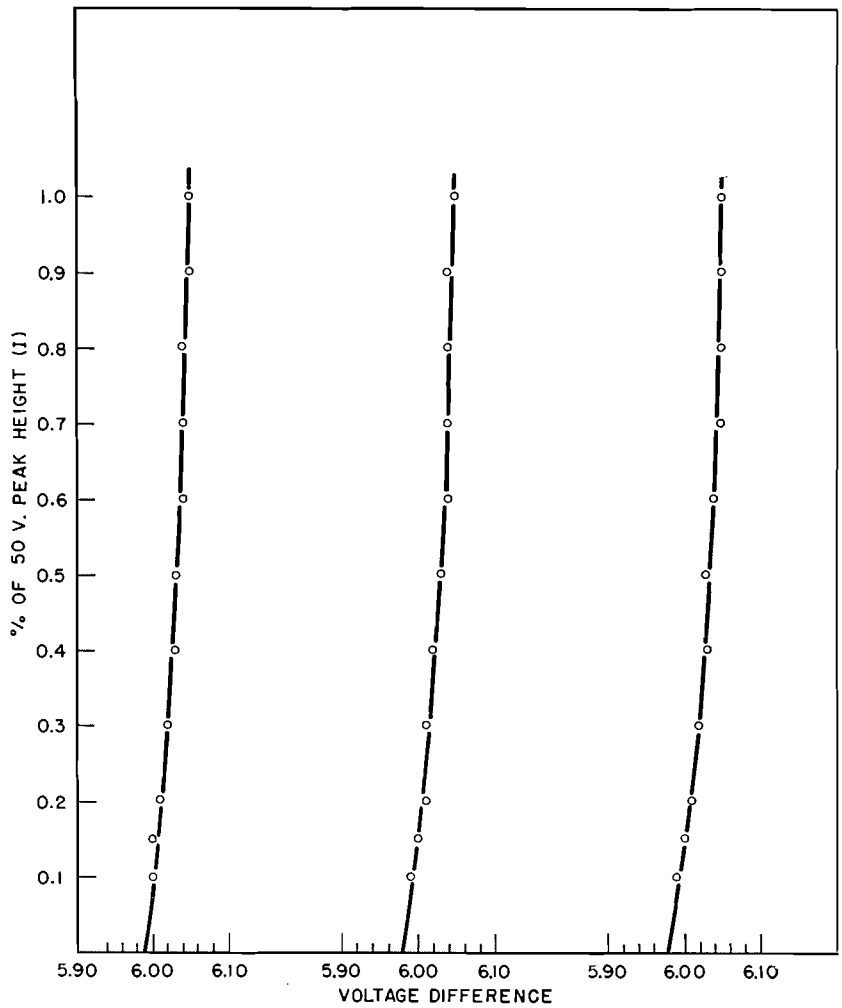

FIG. 2.

carbons isobutene and 2-butene, the values of Honig (7) appear to be the most consistent: I(isobutene) = 9.35 v. and I(2-butene) = 9.29 v. (average). This is a much smaller difference than is found for the radicals. The latter difference is evidently associated with the degree of delocalization energy permitted to the free electron in the two radical configurations. On simple grounds one might expect $I(\beta)$ to be less than $I(\gamma)$ rather than the reverse, since the forms

$$CH_2{=}C(CH_3){-}\dot{C}H_2 \leftrightharpoons \dot{C}H_2{-}C(CH_3){=}CH_2$$

are identical, while those for the γ-radical

$$CH_3{-}CH{=}CH{-}\dot{C}H_2 \leftrightharpoons CH_3{-}\dot{C}H{-}CH{=}CH_2$$

are not. This naive approach is, however, quite inadequate. It is obvious that hyperconjugational effects will be more important in the γ-methallyl radical

than with the β-isomer. This means that the delocalization energy of the γ-radical would certainly be slightly greater than that of the β-isomer; and since it is apparent that there is a definite correlation between the delocalization energy of a molecular species and its ionization potential (15, 2) it is, therefore, to be expected that $I(\gamma\text{-methallyl}) < I(\beta\text{-methallyl})$. This is in agreement with our experimental results.

(*b*) *Appearance Potentials*

The appearance potentials of the β- and γ-methallyl ions from the corresponding iodides are given in Table II. From the relation

$$D(\text{R—X}) \leqslant A(\text{R}^+) - I(\text{R}) \qquad [6]$$

TABLE II

APPEARANCE POTENTIALS AND BOND DISSOCIATION ENERGIES IN METHALLYL IODIDES

Compound	Appearance potential (volts) Individual values	Average	$D(C_4H_7—I)$ (kcal./mole)
β-Methallyl iodide	9.40 9.41 9.40	9.40±0.05	31.6±2
γ-Methallyl iodide	9.15 9.15 9.14	9.15±0.05	33.2±2

the bond dissociation energies given in Table II were derived. The values of $D(C_4H_7—I)$ are almost the same for the two radicals within the experimental accuracy, the γ-methallyl–iodine bond being possibly a little stronger. As would be expected, the bond dissociation energies are only a little lower than the 34–36 kcal. found previously for the allyl–iodine bond (10).

The appearance potentials of the C_4H_7 ion from isobutene and from *cis* and *trans* 2-butene have been reported as follows:

$A(C_4H_7^+)$ from isobutene	11.32±0.1 v.	(22)
$A(C_4H_7^+)$ from *trans* 2-butene	11.24±0.1 v.	(3)
$A(C_4H_7^+)$ from *cis* 2-butene	11.11±0.1 v.	(3)

If it is assumed that the $C_4H_7^+$ ion from isobutene is the β-methallyl ion, a value of $D(\beta\text{-methallyl—H}) = 76\pm3$ kcal./mole is obtained. This is in excellent agreement with the value of 76 kcal./mole suggested by Szwarc (23) on the basis of his work on the 1-butene pyrolysis. Similarly, using the average of the appearance potentials for *cis* and *trans* 2-butene, and assuming that the $C_4H_7^+$ ion produced has the γ-methallyl configuration, $D(\gamma\text{-methallyl—H}) = 80\pm3$ kcal./mole. For comparison with these values, from the pyrolysis of 1-butene D(allyl—H) has been found to be 76.5 kcal./mole and the heat of formation of allyl to be 30 kcal./mole (19). Support for these values can be obtained from recent electron impact data (10) from which

D(allyl—Cl) = 60.4±3 kcal./mole
D(allyl—Br) = 47.7±3 kcal./mole
D(allyl—I) = 35.2±3 kcal./mole (average).

Using the heats of formation for the allyl halides given by Gellner and Skinner (6)

$\Delta H_f°$(allyl chloride) = 0.6±3 kcal./mole
$\Delta H_f°$(allyl bromide) = 12.1±3 kcal./mole
$\Delta H_f°$(allyl iodide) = 22.0±3 kcal./mole

these data lead to the following values of $\Delta H_f°$(allyl)

32.0±6 kcal./mole
33.1±6 kcal./mole
31.7±5 kcal./mole

with an average of 32.3±6 kcal./mole. In view of the good agreement of these results, this limit of error appears to be extreme. From this average value and the heat of formation of propylene (4.88 kcal./mole (18)) the bond dissociation energy D(allyl—H) = 79±6 kcal./mole, in good agreement with the pyrolysis value.

By combining these data with the heats of formation of isobutene (−3.3 kcal./mole) and 2-butene (average of *cis* and *trans* −1.9 kcal./mole (18)), the heats of formation of the radicals are given as:

$\Delta H_f°(CH_2{:}C(CH_3)\dot{C}H_2)$ = 21±3 kcal.
$\Delta H_f°(CH_3CH{:}CH\dot{C}H_2)$ = 26±3 kcal.

A further calculation of interest involves the relation

$$I_{RH} - I_R = D(R—H) - D(R^+—H)\,. \qquad [7]$$

As discussed in an earlier publication (5) the variation of the quantity $I_{RH} - I_R$ with substitution gives a measure of the relative stabilization of the R—H bond in the neutral molecule and the ion. It was found that for benzyl radicals $I_{RH} - I_R$ = 1.47 v., for xylyl radicals ∼ 1.4 v., and for allyl radicals = 1.68 v. From the values of I_{RH} given above, $I_{RH} - I_R$ for β-methallyl = 1.32 and for γ-methallyl = 1.58 v. From equation [7], and assuming that the derived values of D(R—H) in Table III are correct, D(β-methallyl$^+$—H) = 46 kcal./mole and D(γ-methallyl$^+$—H) = 44 kcal./mole.

TABLE III

APPEARANCE POTENTIALS AND BOND DISSOCIATION ENERGIES IN ISOBUTENE AND 2-BUTENE MOLECULES AND IONS

Compound	Appearance potential of $C_4H_7^+$ (volts)	$D(C_4H_7—H)$* (kcal./mole)	$D(C_4H_7^+—H)$* (kcal./mole)
Isobutene	11.32±0.1 (22)	76±3	46
2-Butene	*cis* 11.11 *trans* 11.24 av. 11.18±0.1 (3)	80±3	44

**Assuming the $C_4H_7^+$ ion formed to have the β-methallyl structure from isobutene and the γ-structure from 2-butene.*

TABLE IV

HEATS OF FORMATION OF RADICALS AND IONS

Radical or ion	ΔH_f° (kcal./mole)
$CH_2{:}\,C(CH_3)\dot{C}H_2$	21±3
$CH_3CH{:}\,CH\dot{C}H_2$	26±3
$CH_2{:}\,CH\dot{C}H_2$	32±6
$CH_2{:}\,C(CH_3)CH_2^+$	206±3
$CH_3CH{:}\,CHCH_2^+$	204±3
$CH_2{:}\,CHCH_2^+$	220±6
$CH_2{:}\,C(CH_3)CH_3^+$	212
$CH_3CH{:}\,CHCH_3^+$	212
$CH_2{:}\,CHCH_3^+$	232

In Table IV are listed the heats of formation of the radicals, the radical ions, and the olefin ions, assuming that the electron impact data given above correspond to the assigned dissociation processes.

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ORGANIC DEUTERIUM COMPOUNDS

XV. SYNTHESIS OF SOME DEUTERATED ALKANES[1]

By Mary Elaine Leblanc, A. T. Morse, and L. C. Leitch

ABSTRACT

An improved method of preparing deuterated alkanes from the halides has been developed. Dehalogenation of ethyl iodide, 1,1-dibromoethane, and 1,1,1-trichloroethane with zinc dust in deuterium oxide – dioxane solutions, or even with deuterium oxide alone, gave excellent yields of ethane-d_1, ethane-1,1-d_2, and ethane-1,1,1-d_3. Methane-d_1, -d_2, -d_3, and -d_4 were prepared similarly from methyl iodide, dibromomethane, chloroform, and carbon tetrachloride respectively. The isotopic purity of the products was over 90 mol. %. The reaction is also applicable to higher alkyl halides.

The dehalogenation of alkyl halides has been used only to a limited extent for the preparation of deuterated alkanes. MacWood and Urey (6) synthesized mono-, di-, and tri-deuteromethane from the appropriate halides, deuterium oxide, and aluminum amalgam. The same compounds were later prepared by Benedict, Morikawa, and Taylor (1) by the action of zinc and ethanol-*d* on the polyhalides. Perhaps owing to the presence of ordinary ethanol in the ethanol-*d* none of the products they obtained was isotopically pure. According to Dibeler and Mohler (3) the dehalogenation of bromoform and methylene bromide with lithium aluminum deuteride leads to deuterated methanes which contain up to 40% of the less deuterated species. The action of deuterium oxide on a Grignard reagent has been used to prepare methane-d_1 (2).

Each of these methods has its own peculiar disadvantages. The aluminum–mercury couple used by MacWood and Urey (6) is probably difficult to prepare free of protium without impairing its activity. A serious disadvantage of employing a deuterated solvent such as ethanol-*d* is that it has to be recovered. Besides giving impure products, the method of Dibeler and Mohler (3) requires lithium aluminum deuteride which is still rather expensive. Finally, the decomposition of Grignard reagents is strictly limited to the preparation of monodeuterated hydrocarbons.

The action of zinc dust and acetic acid-*d* on halides was used by Schissler, Thompson, and Turkevich (9) in preference to these other methods to prepare a series of deuterated methanes, ethanes, and propanes. In our experience this method is also unsatisfactory, at least for the preparation of molar amounts of ethane-1,1,1-d_3 from 1,1,1-trichloroethane. Mass spectrometric analysis of successive samples of ethane showed a decrease rather than an increase in deuterium content. This discrepancy between our results and theirs seemed to warrant further study of this reaction.

In our experiments the reaction mixture always darkened as though a by-product were being formed. When a suspension of zinc dust in acetic

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anhydride – trichloroethane was stirred for a few minutes before adding any heavy water the temperature of the reaction mixture rose steadily and finally reached the boiling point. Hydrogen and ethane were evolved and darkening took place. Similar results were obtained when trichloroethane was added to a stirred suspension of acetic anhydride and zinc dust. Evidently a side reaction was taking place which gave rise to an acidic by-product, most likely hydrogen chloride. Elimination of hydrogen chloride as the reaction progressed would account for the observed depletion of the ethane in deuterium. It seemed futile to expect ethane-d_3 of high deuterium content to be formed under these conditions until some means was found of preventing the side reaction. Our next experiments were therefore directed to that end.

We found that the side reaction could be suppressed by adding trichloroethane to acetic acid-*d* in acetic anhydride or dioxane. The acetic acid-*d* was prepared by hydrolyzing the anhydride *in situ* with an equivalent amount of deuterium oxide and a trace of phosphoric anhydride. The yield of ethane-d_3 was 78% but its deuterium content was still far from satisfactory. It started at 21 mol. % CH_3CD_3 and rose slowly with successive samples to 70 mol.%. A slight improvement was observed using anhydrous dioxane as a solvent and less acetic acid-*d*, the purity rising from 51 to 81.8 mol.%.

It has been recently demonstrated (8) that very pure acetic acid-*d* cannot be prepared by hydrolysis of acetic anhydride—even after the latter has been heated under reflux for several days over magnesium turnings. On the other hand acetyl chloride previously distilled over dimethylaniline gives on hydrolysis acetic acid-*d* over 98% pure as judged by the preparation of 95+mol.% toluene-α-d_3 from benzotrichloride (8). However, even acetic acid-*d* prepared in this manner did not give ethane-d_3 as isotopically pure as the toluene-α-d_3. At this point further work with acetic acid-*d* seemed unjustified and we decided to re-examine the other methods of preparing deuterated hydrocarbons.

Dehalogenation with zinc and methanol-*d* (or ethanol-*d*) offered no advantage over the use of acetic acid-*d* for reasons mentioned earlier. Nevertheless, the work of Benedict, Morikawa, and Taylor (1) with this reagent indicated that iodides react with zinc dust in alcohols as well as in acids. Furthermore, MacWood and Urey (6) had shown that bromides and iodides react with water in the presence of aluminum amalgam. It seemed possible that zinc dust might react with halides in deuterium oxide – dioxane solutions and perhaps even with heavy water alone. Experiments first with ethyl iodide, then with ethylidene bromide, and finally with 1,1,1-trichloroethane fully substantiated this inference. Deuterated ethanes of higher purity than had been obtained by other methods were synthesized in good yields by this simplified approach.

This procedure was extended to the preparation in excellent yields of the four deuteromethanes analyzing 96 atom % D from carbon tetrachloride, chloroform, methylene bromide, and methyl iodide. The preparation of homologous deuterated hydrocarbons by this method appears limited only by the availability of the halides.

In the preparation of ethane-1,1,1-d_3 from trichloroethane, zinc, and heavy water, there always remained a small residue after the excess halide was distilled off. A sublimate of white crystals, m.p. 173–4°C., was obtained on distilling the residue under vacuum in a Spath bulb. The melting point of the product was not depressed on admixture of 2,2,3,3-tetrachlorobutane prepared by the chlorination of 2-butyne (7). A high boiling liquid was likewise obtained from the residue from the preparation of ethane-1,1-d_2. Analogy would indicate that this is 2,3-dibromobutane; the quantity isolated was too small to permit adequate characterization. These products are probably formed by doubling. Henne (4, 5) has reported a similar reaction when fluoroiodoethanes are heated with zinc dust in acetic anhydride. This is, however, believed to be the first time such doubling has been reported for chloroethanes.

EXPERIMENTAL

Ethane-1,1,1-d_3

(*a*) *From 1,1,1-Trichloroethane, Zinc, and Acetic Acid-d*

1. The procedure of Schissler, Thompson, and Turkevich (9) was followed but on a larger scale. Acetic anhydride and 1,1,1-trichloroethane were purified by distillation. The anhydride (30 ml.), zinc dust (15.0 gm.), and 1,1,1-trichloroethane (20 ml.) were placed in a 100 ml. round-bottomed flask under a cold finger reflux condenser which was attached to a vacuum line by a side arm. After the apparatus was evacuated deuterium oxide was added in 0.2-ml. portions to the reactants while stirring with a magnetic bar. Samples of deuterated ethane were collected after each addition of heavy water and analyzed by mass spectrometry. The deuterium content of successive samples fell rather than rose. At the same time the reaction mixture darkened considerably. On addition of water at the completion of the experiment a brown gummy polymer was precipitated. Several additional runs were made with the same results.

2. In this experiment acetic anhydride, zinc dust, and 1,1,1-trichloroethane in the same amounts as in (1) were stirred under a reflux condenser in a flask immersed in water overnight. By morning the mixture had turned dark brown. The suspended solid dissolved on adding 75 ml. of water and a brown gum was precipitated. It was not volatile and appeared to be a polymer. Apparently the reagents react before any water is added.

3. A suspension of zinc dust (20 gm.) in acetic anhydride (80 ml.) was stirred for three hours. No gas was evolved during this time. Trichloroethane (8.0 ml.) was then added and the contents stirred while the flask was kept immersed in cold water. A gas was now continuously evolved which condensed in a trap cooled in liquid nitrogen. It was identified by its boiling point as ethane. Yield: 0.4 ml. at −100°C. Addition of more trichloroethane gave 0.8 ml. of ethane. No further evolution of ethane took place on adding water.

4. In this experiment the acetic anhydride (100 ml.) was replaced in part by acetic acid-*d* (20 gm.) which had been prepared by hydrolyzing the anhydride in the presence of a trace of phosphoric anhydride as catalyst. Trichloroethane was then added to the stirred reaction mixture in four portions. The

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yields of ethane-d_3 from 2.0, 3.0, 2.0, and 2.0 ml. of halide were 0.6, 1.1, 0.6, and 0.6 ml. respectively measured at the boiling point. The deuterium content of each sample analyzed by mass spectrometry was 21.5, 31.3, and 53 mol.% CH_3CD_3; the sample of fraction three contained air.

The deuterium content of the ethane now rose rapidly with each fraction collected but in terms of mol.% it was still unexpectedly low.

5. When the acetic anhydride was replaced by anhydrous dioxane (150 ml.) some improvement was noted in the isotopic purity. It started at 51.0 and rose steadily to 83.8 mol.% CH_3CD_3 with successive samples.

6. An experiment was carried out using acetic acid-*d* which had been prepared by hydrolysis of acetyl chloride (8). There was little improvement in the deuterium content over the preceding experiment.

(*b*) *From 1,1,1-Trichloroethane, Zinc, and Deuterium Oxide*

A suspension of 15.0 gm. of zinc dust in 25 ml. of 1,1,1-trichloroethane was stirred in a 100 ml. round-bottomed flask attached through a cold finger condenser to the vacuum line while 4.0 ml. of deuterium oxide (99.6%) was added dropwise over a period of about four hours. The ethane evolved was collected on the vacuum line in a U-tube cooled in liquid nitrogen. The zinc became spongy and after an hour or so it became very difficult to stir the mixture with a magnetic bar. The ethane was purified by two distillations from a trap cooled in liquid nitrogen and slowly warmed to −78°. Yield: 1.6 ml. at −100°C. The mass analysis of this product was 93.5 mol.% CH_3CD_3.

Ethane-1,1-d_2

1,1-Dibromoethane (15.0 ml.) was freed of traces of dissolved hydrogen bromide by distillation through a tube of Ascarite–Drierite on the vacuum line. It was then distilled into a small flask containing 5.0 gm. of zinc dust. Deuterium oxide (3.0 ml.) was then added dropwise from a funnel over a period of three hours to the zinc and halide mixture while stirring. The ethane-1,1-d_2 evolved was collected as described above for trideuteroethane. Yield: 1.0 ml. at −100°C. Mass analysis: 98.7 mol.% CH_3CHD_2.

Ethane-d_1

A suspension of zinc dust (15.0 gm.) in 40 ml. of ethyl iodide was stirred overnight attached to a vacuum line in a flask with a cold finger condenser. By the following morning the zinc had been completely converted into a white solid—zinc ethyl iodide. On adding deuterium oxide dropwise copious amounts of ethane-d_1 were evolved. It was collected and purified as described for trideuteroethane. Yield: 5.4 ml. at −100°C. Mass analysis: 97.0 mol.% C_2H_5D.

Methane-d_4

Deuterium oxide (8.0 gm.) was added dropwise over two hours to a boiling suspension of zinc dust (35 gm.) in carbon tetrachloride (60 ml.). The gases evolved were collected over water or mercury and then condensed in a U-tube cooled in liquid nitrogen on the vacuum manifold. After a small amount of air was pumped off the methane-d_4 was melted and the volume measured. Yield:

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2.0 ml. Mass analysis showed a deuterium content of 97.5 mol.% CD_4 and 2.5 mol.% CD_3H or 99.36 atom % D. Yield: 90% of the theoretical.

Methane-d_3

Chloroform (60 ml.) was freed of traces of ethanol or water by distillation through a U-tube containing phosphorus pentoxide on the vacuum line. A suspension of zinc dust (25 gm.) in the purified chloroform was heated under reflux for one hour on the vacuum line. After traces of ordinary methane in the line were swept out with dry nitrogen, deuterium oxide (6.0 ml.) was added dropwise over a period of two hours. The methane-d_3 evolved was collected and purified as described in the previous example. Mass analysis showed 93.2 mol.% CD_3H, 4.76 mol.% CH_2D_2, and 1.43 mol.% CH_3D or 96.87 atom % D. The yield was nearly theoretical.

Methane-d_2

Deuterium oxide (5.0 ml.) was added slowly to a stirred suspension of zinc dust (18 gm.) in 50 ml. of methylene bromide. The reaction mixture soon became warm and eventually refluxed. The yield of methane-d_2 which was isolated as described in the previous examples was nearly theoretical. The deuterated methane analyzed 93.1 mol.% CH_2D_2, 5.9 mol.% CH_3D, and 1.1 mol.% CH_4 or 96.0 atom % D.

Methane-d_1

Deuterium oxide (3.0 ml.) was slowly added to a stirred suspension of zinc dust (10 gm.) in methyl iodide (30 ml.). The yield of methane-d_1 analyzing 98 mol.% CH_3D was nearly theoretical.

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DETERMINATION OF PARAMETERS IN OVERPOTENTIAL STUDIES[1]

By H. B. Morley[2] and F. E. W. Wetmore

ABSTRACT

A simple method is reported for analyzing decay curves in overpotential studies. As well, equations have been derived for build-up and decay curves and for the overpotential–current relationship, based on an assumption which introduces less error than the simplifying assumptions used previously.

In studies of the behavior of cathodes exhibiting overpotential it has been usual to investigate the variation of the steady state overpotential, η, with applied current density, i, and to report the results in terms of Tafel's equation

$$\eta = a + b.\ln i = b.\ln(i/i_0). \qquad [1]$$

Much less attention has been paid to potential–coulomb build-up curves and to potential–time decay curves. In a recent study of the cathodic behavior of silver in aqueous sulphuric acid solution all three types of determinations were made. A comparison of the results has brought out some points of general interest in the field of overpotential studies.

Examination of the experimental results consistently showed the following behavior. Tafel's equation was found to hold over the entire range of current densities studied (5 to 500 μa. cm.$^{-2}$). Potential–coulomb curves were found to be linear over the first and greater part of the build-up, provided that the solution had been sufficiently purified by pre-electrolysis (2). In the examination of decay curves it was noted that those taken after build-up to the steady state at low current densities could be identically superimposed on those taken after build-up at high current density, simply by adding to the actual time t a quantity θ', as shown in Fig. 1. The upper curve shows the decay of the

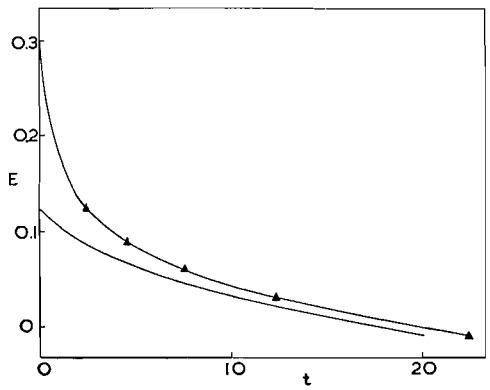

FIG. 1. Decay of cathode potential with time. E is defined as the potential of the reversible hydrogen electrode less the cathode potential (E is positive when the cathode is polarized); t is in seconds. Further details are given in the text.

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Contribution from the Electrochemical Laboratory, University of Toronto, Toronto, Ontario.
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potential of a 111 crystal face after build-up at 118 μa. cm.$^{-2}$. The lower curve corresponds to 4.7 μa. cm.$^{-2}$ and the triangles represent points from the lower curve with $\theta' = 2.3$ sec. added to the actual time t.

The quantity θ' was found to depend, of course, on the initial potentials of both curves involved in the superimposition. Since a decay curve from a large initial potential could be superimposed on one from a still larger initial potential, it was obvious that a value of θ' depending solely on the initial potential of the particular decay curve could be achieved only by superimposition on a curve falling from an infinite initial potential. Such a quantity will be designated by θ, to distinguish it from the directly determinable θ'.

Furthermore, in agreement with the observations of Armstrong and Butler (1), the decaying potential was found to be linear in log t, except for small values of t and E. This, along with the superimposition, suggested that the potential E might be linear in $\log(t + \theta)$, i.e.

$$[2] \qquad dE/dt = -k/(t + \theta).$$

The initial slope of the decay curve would then be $-k/\theta$, from which the value of θ can be derived as follows. The initial rate of build-up can be expressed by the equation

$$[3] \qquad dE/dq = 1/C,$$

in which q is the charge passed and C a constant having the dimensions of capacitance. At any time t after the current is applied,

$$[4] \qquad dE/dt = i/C - k/\theta^*,$$

in which θ^* is the value of θ appropriate to the instantaneous value of E considered as an initial potential in a decay. In the steady state of overpotential

$$[5] \qquad 0 = dE/dt = i/C - k/\theta,$$

in which θ is appropriate to the overpotential, or to the particular current used to produce it. Therefore

$$[6] \qquad \theta = kC/i$$

and θ has the value zero only for the imaginary case of infinite initial potential resulting from an infinite current; it is similar to the constant of integration t' mentioned by Grahame (4).

In effecting the superimposition of one decay curve on another the shift of the time scale, θ', is now seen to be actually $(\theta_2 - \theta_1)$, corresponding to the two current densities i_2 and i_1 used for the build-ups. Hence

$$[7] \qquad kC = (\theta_2 - \theta_1)/(1/i_2 - 1/i_1)$$

and the value of the product kC can be determined from the experimental quantities, θ', i_2, and i_1. Then θ for any value of build-up current can be calculated through equation [6]. Experiment demonstrated the validity of this interpretation.

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With θ known it is of consequence to integrate equation [2] under the condition that $E = \eta$ at $t = 0$ to yield

$$[8] \qquad E = \eta - k.\ln(1 + t/\theta).$$

Thus a decay curve can be plotted as E against $\log(t + \theta)$ to give a straight line of slope $-2.303k$, as shown in Fig. 2 for three current densities. The

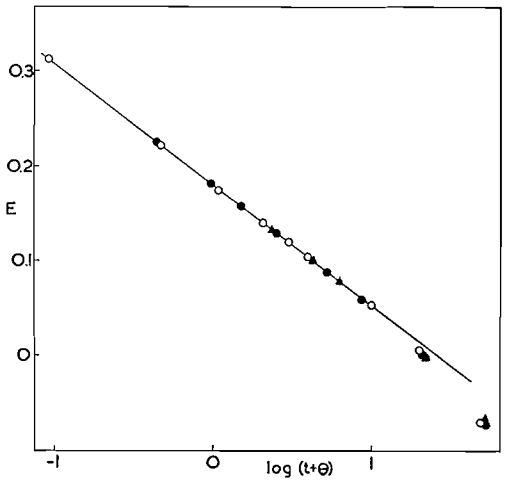

FIG. 2. Decay of cathode potential with time. The open circles refer to a polarizing current of 118, the blackened circles 23.5, the triangles 4.7 μa. cm.$^{-2}$; t and θ are in seconds.

identity of overlapping parts of the three lines shows clearly the accuracy of the superimposition. It should be noted that the value of k so found is much more precise than the value of θ used in the evaluation. As reported earlier (1), the value of k was found to be the same as that of b in the Tafel expression. Use of $\log(t + \theta)$, rather than $\log t$, as the abscissa has the distinct advantage that the curve remains linear even to $t = 0$.

A value of C, of the same precision as θ, can be obtained as $\theta i/k$; as well it can be evaluated from the slope of the linear initial portion of the build-up curve. From equations [1], [4], and [6]

$$[9] \qquad dE/dq = (1/C)[1 - \exp\{(E - \eta)/b\}],$$

which shows that the linearity of the build-up curve is lost as E approaches η. Values of C determined from build-up curves were not the same as those from decay curves; it is conceivable that the latter would be less susceptible than the former to the effects of reduction of constituents other than hydrogen ion.

Use of the analytical quantity θ arose from examination of experimental results, without appeal to mechanism. It is of interest to see how θ fits in with expressions developed from mechanisms involving potential barriers and exchange currents (3). In the mechanistic development the rate of build-up is given by

$$[10] \qquad dE/dt = i/C - (i_0/C)[\exp(E/b) - \exp(-E/b')],$$

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in which i_0 is interpreted as the exchange current density at zero overpotential and the terms b and b' are $RT/\alpha zF$ and $RT/(1-\alpha)zF$, respectively. The rate of decay is given by

$$dE/dt = -(i_0/C)[\exp(E/b) - \exp(-E/b')]. \quad [11]$$

In order to make these expressions more amenable to treatment, simplifying assumptions have been used. One of these (I) is to neglect the second exponential term completely; another (II) is to assume that $\alpha = 0.5$, so that $b = b' = 2RT/zF$. The latter assumption is always of doubtful validity. Assumption (I) will have no appreciable effect on build-up curves, except at extremely low current densities, and will be in error for decay curves only as E approaches zero. Use of (I) gives the slope of the decay curve as

$$dE/dt = -(i_0/C).\exp(E/b),$$

which on integration under the condition that $E = \eta$ at $t = 0$ yields equation [8]. Thus it is clear that use of θ embraces assumption (I). The distinction between equation [11] and the same modified by (I) becomes apparent only as E approaches zero. For purposes of determining b and C, equation [8] is satisfactory at values of i greater than $10i_0$.

An assumption more general and precise than either (I) or (II) is to take $b = b'$, without assuming a particular value of b and without neglecting the second exponential term completely. From assumption (III) it follows that the slope of the build-up curve is

$$dE/dt = i/C - (2i_0/C).\sinh(E/b), \quad [12]$$

that of the decay curve

$$dE/dt = -(2i_0/C).\sinh(E/b), \quad [13]$$

and the expression replacing that of Tafel is

$$\eta = b.\sinh^{-1}(i/2i_0). \quad [14]$$

Equation [12] shows that the build-up curve will be linear so long as $(2i_0/i).\sinh(E/b)$ is small in comparison with unity. Integration of equation [12] yields a cumbersome expression, but integration of equation [13] gives

$$\ln\coth(E/2b) = \ln\coth(\eta/2b) + 2i_0t/bC, \quad [15]$$

which suggests a convenient form for extrapolating decay curves to zero time. Since only the precisely determinable quantity b (k in equations [2] to [8]) is required to make the plot of $\log\coth(E/2b)$ against t, this form may have some advantage over equation [8]. Equation [14] differs from equation [1] only at very small values of i/i_0, for which it leads to the condition that $\eta = 0$ when $i = 0$.

The quantity θ can be derived from equation [15] in the form

$$t = (bC/2i_0).\ln[\coth(E/2b)/\coth(\eta/2b)].$$

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By definition, θ is the time required for the potential to fall from infinity to E, less the time for a finite potential to fall to the same value E. Hence

$$\theta = (bC/2i_0) \cdot \ln[\coth(\eta/2b)]. \quad [16]$$

Although there appears to be little resemblance between the members of the pairs of equations [1] and [14], [6] and [16], and [8] and [15], it will be found that they are arithmetically identical under the usual experimental conditions, in which i is substantially greater than i_0.

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APPLICATION OF THE ARCHIBALD ULTRACENTRIFUGAL PROCEDURE TO LYSOZYME AND APURINIC ACID: EVALUATION USING A MECHANICAL INTEGRATOR[1]

By David B. Smith, G. C. Wood,[2] and P. A. Charlwood

ABSTRACT

The method outlined by Archibald for handling transient data in equilibrium ultracentrifugation yields a molecular weight for lysozyme that conforms to those given by other methods. A method for applying the Archibald procedure to apurinic acid which is polydisperse and has a concentration dependent sedimentation rate is outlined. The use of a mechanical integrator for reducing the computational work is described.

Advantages of the sedimentation equilibrium method of molecular weight determination include soundness of theory, wide molecular weight range covered, and the small amount of material (2–3 mgm. in conventional ultracentrifuges) required. A disadvantage has been the prolonged centrifuging time involved. Archibald (1), however has shown that molecular weights and information on homogeneity may be obtained from the concentration distribution in the ultracentrifuge cell before equilibrium is attained.

Archibald's method has been tested (4) on a saponin, digitonin, molecular weight 1229.3, and also (8) on raffinose, molecular weight 504.5, and bovine serum albumin. Porath (9) has used the method to obtain the molecular weight of bacitracin.

This communication records the testing of Archibald's method on lysozyme whose molecular weight, 14,100±500 (6), is well defined. The procedure has been extended to deal with a preparation of apurinic acid which shows, besides polydispersity, some concentration dependence of the sedimentation rate. The computational work may be greatly reduced by the use of a mechanical integrator.

The distribution of solute in the ultracentrifuge cell at equilibrium is given by

$$\frac{1}{rc}\frac{dc}{dr} = \frac{M(1-\bar{v}\rho)\omega^2}{RT} = \frac{\omega^2 S}{D} = \delta$$

where c is the concentration at distance r from the center of rotation, M is the molecular weight, $\bar{v}$ the partial specific volume, ρ the density of the medium, ω the angular velocity, R the gas constant, T the absolute temperature, S the sedimentation coefficient, and D the diffusion coefficient. Sedimentation and diffusion rates are assumed to be independent of concentration. Archibald showed that the function $(1/rc)(dc/dr)$ at the meniscus of the solution and at the base of the cell is equal to δ at all times and that values of $(1/rc)(dc/dr)$

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found experimentally in regions near base and meniscus at any given time may be extrapolated to these limits to obtain δ_b and δ_m respectively. If the solute is monodisperse, δ_b and δ_m are equal and proportional to M. In polydisperse solutions, δ_b is higher than δ_m and each value is proportional to the weight-average molecular weight at base and meniscus respectively.

However, if the usual type of concentration dependence of the sedimentation rate exists, the values of δ obtained will be too low especially at the base where the higher concentration results in greater depression of S. Equality of the two values of δ does not therefore indicate monodispersity if the sedimentation rate is concentration dependent. The concentration dependence of D is normally much less than that of S, since a thermodynamic factor related to the second virial coefficient usually tends to oppose the hydrodynamic factor (11). These concentration effects can be eliminated by extrapolation to zero concentration.

Application of the Archibald method requires a knowledge of dc/dr and c at points at and close to meniscus and base. The usual diagonal schlieren method of observing refractive index gradients in the ultracentrifuge cell gives a pattern that may be taken to be a plot of dc/dr vs. r. The arithmetic evaluation of c as a function of r from such a plot is tedious and this fact has hindered the application of Archibald's procedure. The operation may be greatly simplified by the use of a mechanical integrator capable of measuring first and second moments besides areas. For this method, the equations of Brown, Kritchevsky, and Davies (4) were transformed as follows:

$$c_b - c_m = \int_{r_m}^{r_b} \frac{dc}{dr}\,dr$$

$$\int_{r_m}^{r_b} r\,c\,dr = \tfrac{1}{2}\left[c_b r_b^2 - c_m r_m^2 - \int_{r_m}^{r_b} r^2 \frac{dc}{dr}\,dr\right] = \frac{c_0}{2}\left[r_b^2 - r_m^2\right]$$

where r is the distance in cm. from the axis of rotation, c the corresponding concentration, c_b and c_m the concentrations at the base and meniscus, r_b and r_m respectively, and c_0 the initial concentration of the solution.

Concentrations c_b and c_m can thus be obtained from the area of the pattern and its second moment about the axis of rotation

$$\int_{r_m}^{r_b} r^2 \frac{dc}{dr}\,dr,$$

together with the other known or measurable quantities.

The second moment of part of the ultracentrifuge pattern about the axis of rotation enters the equations used by Baldwin (2) and by Klainer and Kegeles (8). Here too mechanical integration would simplify the computations.

MATERIAL AND METHODS

Lysozyme (Armour Lot No. 003L1) was examined in sodium phosphate buffer pH 6.6, ionic strength 0.2.

Apurinic acid prepared (12) from calf thymus sodium desoxyribonucleate was dissolved in sodium acetate buffer pH 5.0, ionic strength 0.15.

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Refractive index increment, dn/dc, of lysozyme is 1.88×10^{-3} ml. gm.$^{-1}$ (7). The value assumed for apurinic acid was that reported (10) for sodium desoxyribonucleate, also 1.88×10^{-3} ml. gm.$^{-1}$.

Partial specific volume, $\bar{v}$, of lysozyme is 0.688 ml. gm.$^{-1}$ (6). For apurinic acid, the value 0.55 ml. gm.$^{-1}$ was used. This value has been reported for sodium desoxyribonucleate (5).

The Spinco Model E ultracentrifuge using the standard cell was run at 12,590 r.p.m. Several photographs taken at different bar angles immediately after the rotor had attained full speed provided base lines since it was found that no detectable sedimentation of the buffer salts occurred over 18 hr.

Initial and final temperatures of the rotor differed by about 2° and the average value was used in subsequent calculations.

The optical system of the ultracentrifuge was calibrated by measuring the area of the pattern given by a boundary between a KCl solution and water in the Spinco synthetic boundary cell. The refractive index difference across this boundary was determined in a differential refractometer (3).

The ultracentrifuge patterns were enlarged at measured magnification (about 8×) and traced onto graph paper. The tracings were bisected, base lines were superposed, and the resulting outlines were analyzed both by the arithmetical method of Brown *et al.* (4) and by the use of an Amsler integrator, Type 626. Since the enlarged pattern is too large for the desired second moment to be obtained directly, the instrument was set on an axis parallel to the meniscus at a distance r_e from the center of rotation and chosen so as to approximately halve the outline. The second moment about the axis of rotation is

$$A\,r_e^2 + 2M\,r_e + I = I_0$$

where A is the area of the outline and M and I are its first and second moments respectively about the arbitrary axis.

RESULTS AND DISCUSSION

Lysozyme is an example of a material having relatively uncomplicated sedimentation behavior. Fig. 1 shows a set of ultracentrifuge patterns obtained

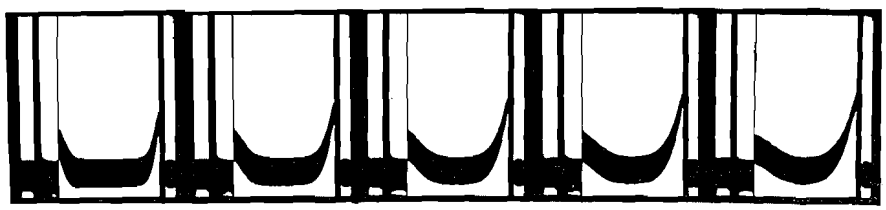

FIG. 1. Ultracentrifuge patterns obtained with lysozyme, initial conc. 1.06%. Sedimentation from left to right. Photographs taken at 58, 148, 238, 328, and 418 min. after attaining full speed.

with lysozyme. Fig. 2 shows a family of curves obtained by the arithmetical method of $(1/rc)(dc/dr)$ plotted against r. In Table I are shown values of δ obtained by both methods of computation after two separate runs with

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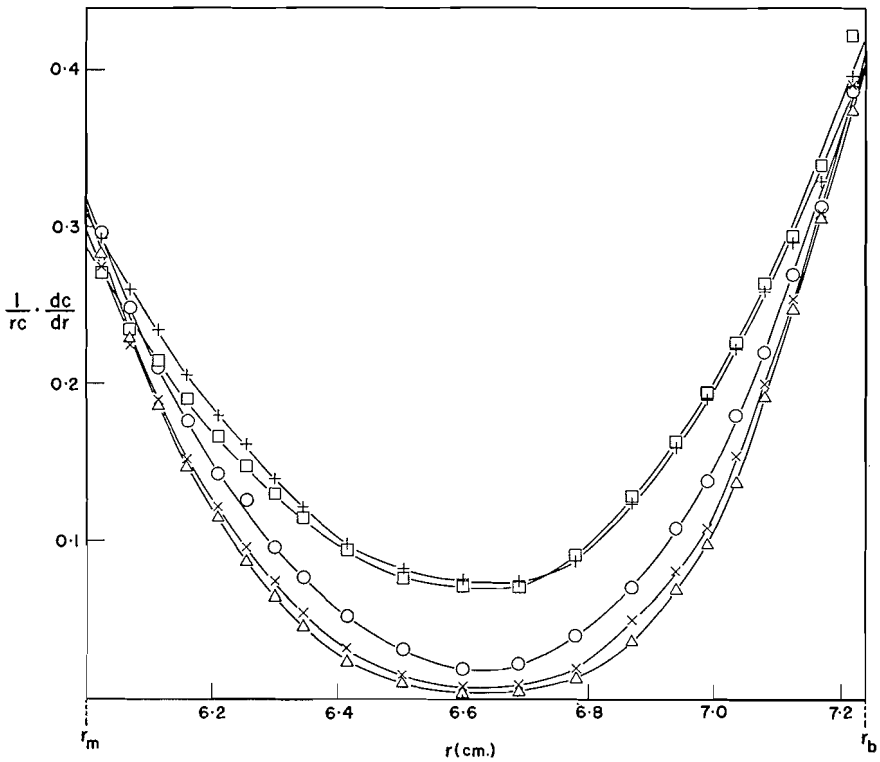

FIG. 2. Values of $(1/rc)(dc/dr)$ computed from ultracentrifuge patterns with lysozyme, initial conc. 1.57%, plotted against distance from axis of rotation. Photographed at 427 (△), 491 (×), 619 (○), 1061 (+), and 1084 (□) min. after attaining full speed.

lysozyme. The values from the arithmetical method are the intercepts at r_m and r_b of extrapolated curves of $(1/rc)(dc/dr)$ against r. The values obtained using the integrator are calculated from the determined values of c_m and c_b, the measured value of r_m, the value of r_b supplied by Spinco, and the values of dc/dr measured at r_m and r_b (extrapolation of the pattern to the latter point is required).

TABLE I

MOLECULAR WEIGHT OF LYSOZYME BY THE ARCHIBALD PRODEDURE

Run 1, c_0 = 1.06%					Run 2, c_0 = 1.57%				
Time (min.)	Arithmetic method		Integrator		Time (min.)	Arithmetic method		Integrator	
	δ_m	δ_b	δ_m	δ_b		δ_m	δ_b	δ_m	δ_b
58	0.32	0.33	0.32	0.35	427	0.32	0.40	0.31	0.42
148	0.30	0.35	0.30	0.37	491	0.30	0.41	0.29	0.41
238	0.29	0.34	0.31	0.37	619	0.32	0.40	0.31	0.42
328	0.31	0.35	0.30	0.38	1061	0.31	0.41	0.30	0.40
418	0.32	0.37	0.30	0.38	1084	0.29	0.42	0.28	0.37
Mean	0.31	0.35	0.31	0.37		0.31	0.41	0.30	0.40
Mol. weight	14,100	16,000	14,100	16,800		14,100	18,700	13,700	18,200

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Molecular weights calculated from δ_m are in excellent agreement with that obtained by Colvin (6), 14,100±500, from separately determined S and D coefficients. The higher values calculated from δ_b may indicate the presence of small amounts of higher molecular weight contaminants from the egg-white source or may be due to concentration effects. The concentration at the base of the cell ranged between about 1.3 and 1.8% in Run 1 and 2.5 and 3.1% in Run 2. These concentrations are outside the range over which Colvin found no dependence of S on concentration. In any case, at these higher concentrations, it is unlikely that the sedimentation rate of lysozyme is greatly reduced. Light scattering measurements by Halwer, Nutting, and Brice (7) indicate that the second virial coefficient of lysozyme is appreciably negative in a medium of pH 6.2 and $\mu = 0.1$. A negative virial coefficient tends to reduce the diffusion coefficient at finite concentrations (11) and thus increase δ. The extrapolation necessary because the region close to the base is not recorded on the photographic plate introduces further error in the estimation of δ_b.

Preparations of apurinic acid are very heterogeneous (12). Fig. 3 shows a family of $(1/rc)(dc/dr)$ vs. r curves for a preparation of this material. The intercepts, δ_m and δ_b, are not the same. Moreover, sedimentation velocity

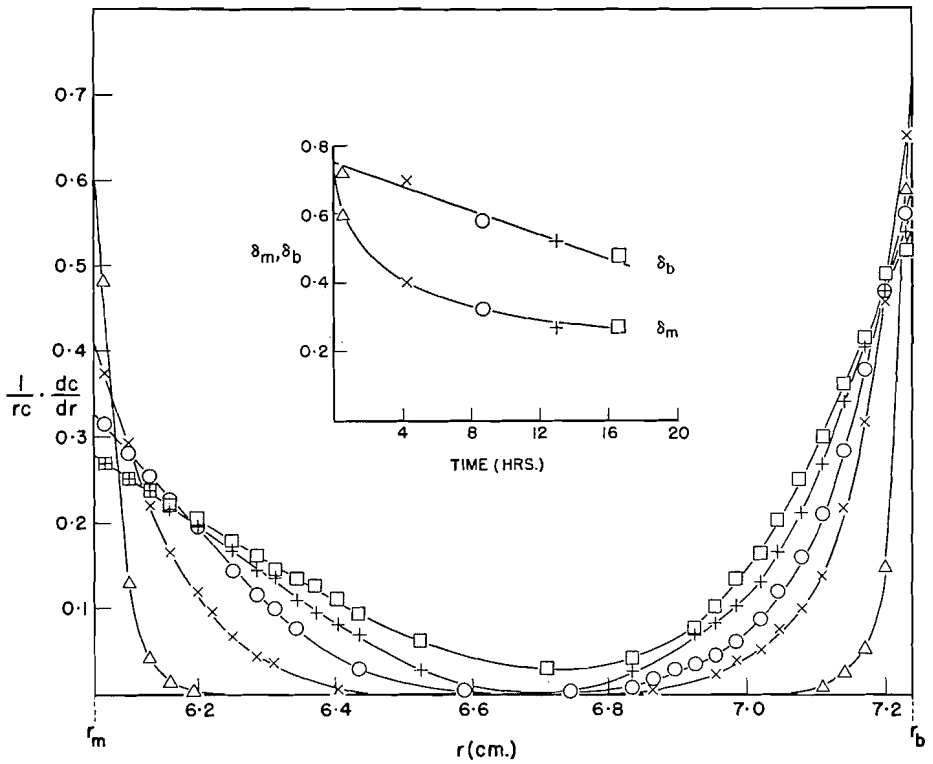

FIG. 3. Values of $(1/rc)(dc/dr)$ computed from ultracentrifuge patterns obtained with apurinic acid, initial conc. 0.53%, plotted against distance from axis of rotation. Photographed at 30 (△), 252 (×), 522 (○), 786 (+), and 1019 (□) min. after attaining full speed.
Inset: Variation of δ_b and δ_m with time.

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determinations on apurinic acid (12) show that its sedimentation rate has a concentration dependence of about 0.1 dl. gm.$^{-1}$ Sved.$^{-1}$. The negative slope of the δ_b vs. time curve (Fig. 3 inset) must arise from the depression of S as the concentration at the base rises since it has been found (12) that instability of the material can have only a small effect.

The concentration effect was eliminated by doing several ultracentrifuge experiments at different initial concentrations, and taking photographs at the same times (t) in each run. For each value of t, δ_b and δ_m were plotted against c_b and c_m respectively and the curves extrapolated to zero concentration to give $\delta_b(c \rightarrow 0)$ and $\delta_m(c \rightarrow 0)$. Since $\delta_b(c \rightarrow 0)$ was found to be greater than $\delta_m(c \rightarrow 0)$, indicating polydispersity, graphs of $\delta_b(c \rightarrow 0)$ and $\delta_m(c \rightarrow 0)$ against t were extrapolated to zero time, as suggested by Archibald, to give $\delta(c \rightarrow 0)(t \rightarrow 0)$ from which the weight-average molecular weight of the unfractionated material was calculated. The two extrapolations may conveniently be done on the same graph (Fig. 4) by plotting δ_b against $(c_b + 0.1t)$

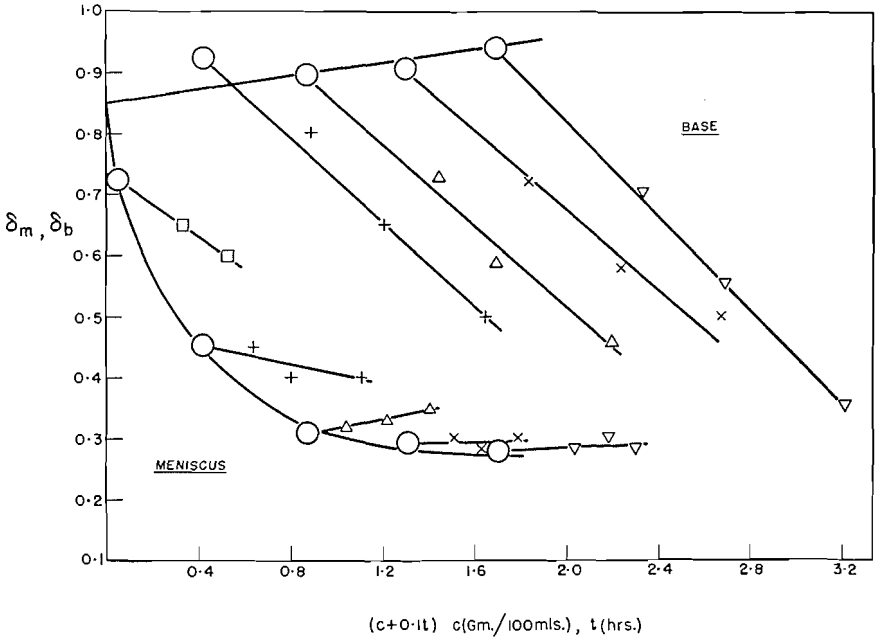

FIG. 4. Values of δ obtained from three ultracentrifuge runs with apurinic acid plotted against $(c + 0.1t)$, showing extrapolation to zero concentration and zero time. Photographs taken at 30 (□), 252 (+), 522 (△), 786 (×), and 1019 (▽) min. after attaining full speed.

and δ_m against $(c_m + 0.1t)$. The weight-average molecular weight, 27,000, is in good agreement with the value of 25,000 found by the light-scattering methods (12). The concentration dependence of δ_b is much greater than that of δ_m, because the species of highest molecular weight, whose sedimentation rates will be most dependent on concentration, tend to concentrate near the base. The value approached by δ_m as centrifugation proceeds corresponds to a molecular weight of 7000.

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Extrapolation of plots of $1/\delta$ against concentration to zero concentration, corresponding to the linear relation between reciprocal sedimentation coefficient and concentration, may be preferable to the above treatment, where higher degrees of concentration dependence are involved.

CONCLUSION

This work has shown that the Archibald method gives molecular weight values for low molecular weight proteins that compare favorably with values obtained in other ways. A method for getting information on size and polydispersity for systems showing concentration dependence of the sedimentation rate has also been outlined. The computational work can be greatly reduced by the use of mechanical integration which also permits ready replication and reduces the opportunity for arithmetic error.

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A LOW-TEMPERATURE APPARATUS FOR SINGLE-CRYSTAL X-RAY GONIOMETERS[1]

By T. T. Harding[2]

ABSTRACT

An apparatus is described which may be used to grow and maintain single crystals at temperatures down to approximately −180°C. The crystals may be grown directly upon the head of the X-ray goniometer in order to permit the recording of data required for the investigation of the crystalline structure of substances which exist in the liquid or gaseous states at ordinary temperatures.

INTRODUCTION

Recent interest in the study of crystal structures of solids at low temperatures and of compounds which exist in the liquid state at ordinary temperatures has led to the construction of a number of low-temperature devices for powder and single-crystal X-ray goniometers (1–18). In this paper an apparatus is described which has been used successfully in a determination of the crystal structure of acetonitrile. This apparatus bears some similarity to that constructed by Owen and Williams (8).

CONSTRUCTION

The crystal is maintained at low temperatures by a stream of dry gas which is cooled by passage through a cooling chamber containing liquid nitrogen. The source of supply of dry gas may vary according to the availability of material, but during operation in this laboratory large amounts of liquid nitrogen were readily available and were used to supply dry nitrogen to the cooling system. A diagram of the gas circuit is shown in Fig. 1.

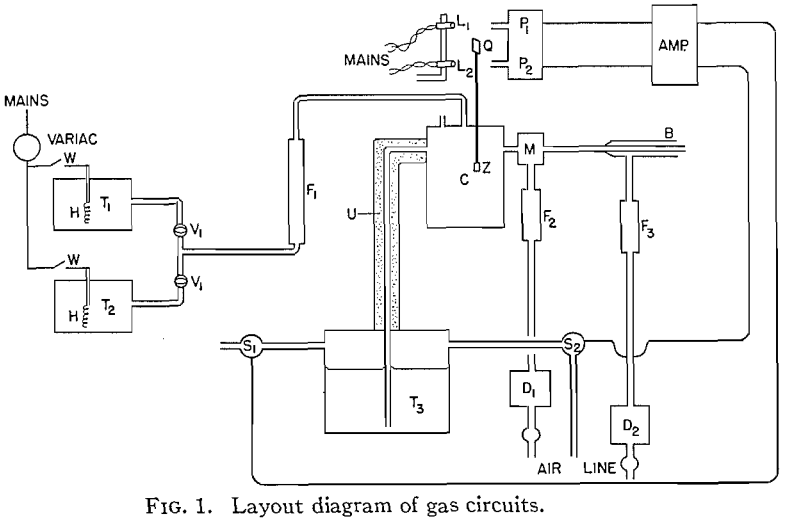

FIG. 1. Layout diagram of gas circuits.

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[2]*National Research Council of Canada Postdoctorate Fellow 1954–55.*

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Dry nitrogen was obtained by boiling liquid nitrogen in one of the large 50 liter dewar tanks T_1 and T_2 using electric heaters H, of 30 ohm resistance operating on mains current (110 volts). The current through the heaters and thus the flow of gaseous nitrogen was regulated by a variac. A constant flow of gas may be maintained when changing from tank T_1 to tank T_2 by opening and closing the appropriate valves V_1 together with the switches W and by adjusting the variac. The flow of gas through the system is indicated by a flowmeter F_1. The gas then passes into the cooling chamber C where it is cooled by liquid nitrogen, and into the mixing head M before being expelled through the delivery tube B to impinge upon the sample tube which is mounted on the goniometer head. In order to maintain a fairly high gas flow-rate around the crystal when the apparatus is operating in its higher temperature range and to assist in temperature control and variation, warm air is passed through a regulating valve through a series of drying agents D_1, including potassium hydroxide to remove carbon dioxide, and a flowmeter F_2 into the mixing head M. Here it is mixed with the cold nitrogen and then expelled through the delivery tube B.

In order to prevent ice formation around the sample tube and goniometer head a stream of air is passed through a regulating valve, a series of drying tubes D_2, and a flowmeter F_3, and finally into a tube mounted coaxially around the delivery tube so that a column of warm dry air surrounds the cold gas stream and serves to prevent ice formation.

The cooling chamber is shown in detail in Fig. 2. Nitrogen gas enters through the tube N and passes through the brass chamber H′ into the large dewar vessel R containing liquid nitrogen. Chamber H′ serves as a collecting point for any impurities in the incoming gas which are deposited on cooling and which may be removed after an experimental run by removing a plug at the bottom of the chamber; this is important when the source of cooling gas is other than liquid nitrogen. The nitrogen then passes from H′ into a coil of copper tubing C, consisting of 15 turns of $\frac{3}{8}$ in. diameter copper with a wall thickness of 1/32 in. The inside diameter of the coil is $3\frac{5}{8}$ in. It was found that the above dimensions for the cooling coil were the most satisfactory for cooling the gas without liquefying it. The cold nitrogen gas passes from the dewar vessel and cooling coil via the tube O into the mixing head M which is constructed with dewar walls. Here the cold gas may be mixed with warm air which enters through the tube O′ before being expelled into the delivery tube B. The dewar vessel R, encased in felt K, is placed in a copper container N. The mouth of the dewar is sealed by a lid J and cork I through which pass the inlet and outlet tubes etc., and a gas outlet X.

The level of the cooling liquid in the dewar vessel R is maintained by means of the following device. A float Z operating in a Pyrex glass tube within the dewar is connected by a fine wire to a shutter of brass foil Q within the closed glass system E which may be dismantled at the ground glass joints G_1 and G_2. The float and shutter rise or fall with the level of liquid in the dewar, the shutter Q being arranged to operate between the two lamps L_1 and L_2 and the photoelectric cells P_1 and P_2 which are connected via the amplifier AMP and

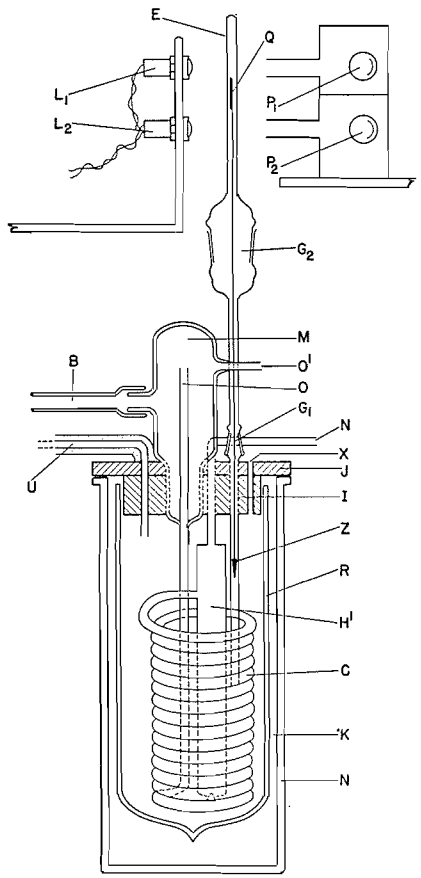

FIG. 2. The cooling chamber.

relays (see Fig. 1) to two solenoid valves S_1 and S_2 respectively. The circuit is arranged so that as the shutter Q falls, it covers the aperture of photocell P_2 and then uncovers it. The amplified impulse from the photocell opens the solenoid valve S_2 which admits air under pressure to the liquid nitrogen reservoir T_3 and forces the liquid into the dewar vessel through the lagged tube U, solenoid valve S_1 being closed. As the level of liquid rises, the shutter covers photocell P_1 and then uncovers it. The resulting impulse closes valve S_2 and opens S_1 to allow the excess pressure to escape from the reservoir T_3, and hence the flow of liquid nitrogen to the dewar vessel R ceases. It may be seen that the constant level device would operate efficiently with only one photocell coupled to a double-pole, double-throw relay. However the electronic arrangement described above was available from an experimental arrangement of a different type which was no longer required.

The construction of the delivery tube shown in Fig. 3 is similar to that described by Burbank and Bensey (2). It consists of a glass dewar-walled central tube of internal diameter 1.0 cm. which is enlarged at one end to fit the

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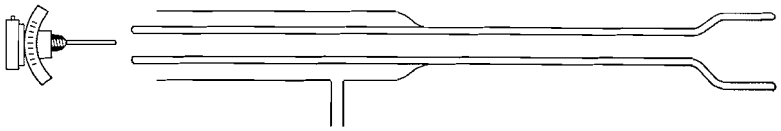

FIG. 3. Delivery tube.

exit tube of the mixing head (see Fig. 2). The nozzle of the delivery tube extends 0.6 cm. beyond the end of the outer jacket of inside diameter 2.5 cm. through which warm dry air is passed via D_2 and F_3 as shown in Fig. 1. It is important that the seal of the double-walled delivery tube should be smooth and well-rounded so that the flow of both columns of gas is as nearly streamline as possible. This ensures that the inside column of cold nitrogen is in contact only with dry air so that ice formation is prevented.

NOTES ON OPERATION AND POSSIBLE MODIFICATION

When in operation the delivery tube is mounted so that the stream of cold gas impinges upon the capillary tube containing the sample for examination. Care must be taken in using the precession goniometer that rotation of the camera through a $\bar{\mu}$ angle of 30° is not prohibited by the position of the delivery tube. Crystals may be grown by controlled cooling and warming of the liquid sample using the valves and flowmeters in the gas circuit to regulate the temperature of the gas impinging upon the sample tube. By noting the readings on the flowmeters the conditions of a particular experiment may be repeated precisely at a later date, or by using a thermocouple mounted upon the goniometer head in the position usually occupied by the crystal the rates of flow of cold gas may be calibrated against temperature. It was also found during operation that it was advisable to use a tube of indicating 'drierite' as the final drying agent in each drying system so that it was possible to have adequate warning when fresh drying agents were required. This was of particular importance in the drying tubes D_2 if ice formation around the specimen was to be prevented. During operation at −70°C. with a cooling stream of gas flowing at 0.5 cu. ft. per min. it was found that 50 liters of liquid nitrogen were sufficient for at least 48 hours' supply of gas whilst a further 50 liters were expended each 24 hr. as cooling liquid. Temperatures down to −180°C. were obtained using higher flow rates and could be maintained without difficulty without too much attention to the liquid nitrogen supply since it is possible to couple any number of reservoirs to the system. It may also be possible to achieve greater economy in the use of liquid nitrogen by making vacuum-jacketed connections between the reservoirs T_1 and T_2 and the cooling chamber. As previously pointed out, the gas supply to this apparatus may be varied according to the availability of materials. Some experiments were undertaken using banks of nitrogen cylinders. This was satisfactory when pure nitrogen was used and then passed through drying tubes containing 'drierite' and potassium hydroxide in order to remove final traces of moisture and carbon dioxide before the cooling chamber was reached. It is also suggested that the gas may be more con-

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veniently supplied by an air pump driving air through agents for the removal of moisture and carbon dioxide. Liquid air may then be used as the cooling agent.

It was found that the apparatus described above would maintain low temperatures for an indefinite period.

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REACTIONS OF SOME HALOGEN DERIVATIVES OF TETRAHYDROPYRAN-2-OL[1]

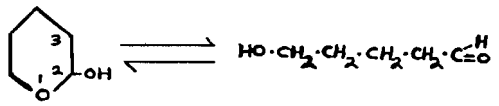
By E. H. Charlesworth and A. Giesinger

ABSTRACT

The 3-halotetrahydropyran-2-ols have been found to readily give derivatives of tetrahydrofurfural in aqueous alcohol under weakly basic or acidic conditions. In strongly alkaline solution tetrahydropyran-2,3-diol and its anhydro-polymers were formed. 3,3-Dichlorotetrahydropyran-2-ol and 2,3,3-trichlorotetrahydropyran have been converted by aqueous alkali to viscous sirups which appear to contain 2-hydroxytetrahydropyran-3-one and its tautomers. On oxidation with permanganate these sirups have yielded succinic acid.

INTRODUCTION

The aldehydic properties of tetrahydropyran-2-ol (I) were explained by Paul (7, 9) on the assumption that it existed in equilibrium with δ-hydroxyvaleric aldehyde (II). Paul's view has since been confirmed by other workers,



I II

particularly Schniepp and Geller (14) and Woods and Sanders (17). The latter authors obtained a crystalline 2,4-dinitrophenylhydrazone.

The 3-halotetrahydropyran-2-ols (IV), readily prepared by the hydrolysis of the corresponding 2,3-dihalides (III) in the presence of mild alkaline reagents, have been reported by Paul (8, 10, 11), by I.G. Farben (5), and by Hawkins and Bennett (1, 2). As these possess some aldehydic properties, it has been assumed that they exist in equilibrium with a δ-hydroxyvaleric aldehyde form (V). Crystalline derivatives, however, are not reported, although Paul (11) did isolate a liquid oxime of tetrahydrofurfural following the hydrolysis of the 2,3-dichloride. Paul (9) found that 3-bromotetrahydropyran-2-ol reacted rapidly with phenylhydrazine, but gave only crystals of phenylhydrazine hydrobromide. This latter reaction suggests that in the presence of an organic base the bromohydrin loses hydrogen bromide more rapidly than it acts as an aldehyde.

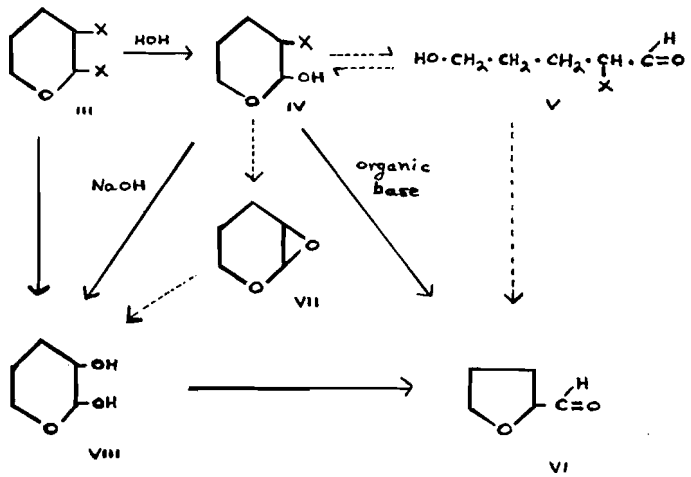
In view of their undoubted aldehyde properties, it seemed desirable to prepare crystalline derivatives of these halotetrahydropyranols and thus to determine the nature of the aldehydic substances derived from them. Both the chloro- and bromo-tetrahydropyranol were found to react with substituted phenylhydrazines to yield the same halogen-free derivatives, namely,

(i) a 2,4-dinitrophenylhydrazone, m.p. 133–134°;
(ii) a 2,4-dinitrophenylosazone, m.p. 242°;

[1]*Manuscript received November 14, 1955.*
Contribution from the Department of Chemistry, the University of Manitoba, Winnipeg, Man. This paper was read before the XIVth Congress of the International Union of Pure and Applied Chemistry in Zurich.

(iii) a *p*-nitrophenylhydrazone, m.p. 146°;
(iv) a *p*-nitrophenylosazone, m.p. 246°;
(v) a *p*-benzylphenylhydrazone, m.p. 74–75°.

In all cases these derivatives are identical with corresponding products made from an authentic sample of tetrahydrofurfural (VI) prepared by the method of Scheibler, Sotscheck, and Friese (13). Hurd and Edwards (3) obtained the same derivatives from tetrahydrofurfural produced by heating tetrahydropyran-2,3-diol (VIII) under reduced pressure.



The 3-halotetrahydropyran-2-ols lose hydrogen halide so readily that they can be titrated with aqueous sodium hydroxide. In each case it is possible to isolate a quantitative yield of the sodium halide salt. We had hoped at first to use this method to obtain the oxide (VII). However, in view of the fact that an organic base when extracting hydrogen halide leaves tetrahydrofurfural as a residue, it seemed that the effect of sodium hydroxide might be the same and thus represent a convenient method of preparing tetrahydrofurfural.

The organic product from the reaction proved to be rather elusive. Organic solvents do not extract it in appreciable amounts from the aqueous mixture. Even continuous extraction proved inadequate. The water had to be removed almost completely, either by absorption on drying agents or better by evaporation, before the product could be taken up in organic solvent.

The nature of the product varies somewhat according to the conditions. If the reaction mixture is kept near room temperature throughout the process, a considerable portion of the product is soluble, with some difficulty, in ether. This ether-soluble substance is aldehydic, but it is a higher boiling liquid than tetrahydrofurfural. It gives the same dinitrophenylosazone, m.p. 242°, as tetrahydrofurfural, but not the phenylhydrazone obtainable from that substance. It readily reduces periodic acid to iodate and forms a 3,5-dinitrobenzoate, m.p. 174°. This substance seems to be tetrahydropyran-2,3-diol (VIII), which Hurd and Kelso (4) prepared by hydrogen peroxide oxidation of dihydropyran.

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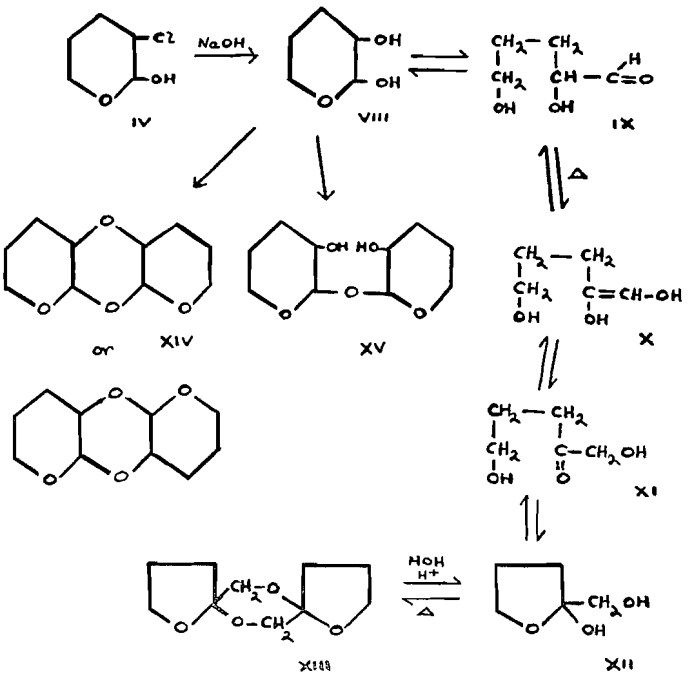
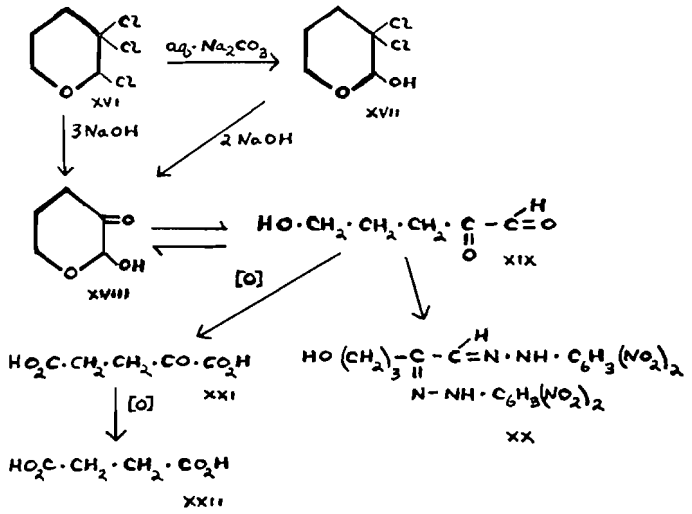
At higher reaction temperatures less of the product is ether-soluble. Small fractions can be extracted with other solvents, but the bulk is soluble only in alcohol and water. Evaporation of the solvent in each case leaves a high boiling sirup which is not easily purified by distillation. In one case a solid, m.p. 190°, precipitated from aqueous solution. In another case a chloroform extract yielded a solid, m.p. 101–102°. The properties of these substances indicate that they are the same $C_{10}H_{16}O_4$ materials as are reported by Hurd and Edwards (3), who obtained them by heating tetrahydropyran-2,3-diol. The lower melting of these two compounds was also obtained by Swadesh and Dunlop (16) from another source. The two groups of workers seem to agree that it has the structure XIII and that it is formed from the diol by the route shown. The structure of the higher melting compound has not been established, but the indications are that it may be XIV. Compound XV has been isolated by Hurd and Kelso (4). Our high boiling sirups are probably mixtures of compounds XIII, XIV, and XV and perhaps more complex structures.



No material was isolated that seemed to be the oxide (VII). If formed at all, it was apparently unstable and hydrolyzed to form the diol (VIII). Other attempts by Paul and Tchelitcheff (12) and by Hurd and Edwards (3) to obtain the oxide have not been too successful.

3,3-Dichlorotetrahydropyran-2-ol (XVII) is mentioned briefly in the literature in a wartime I.G. Farben report (6) and in a German patent (18). We have prepared this substance by warming the 2,3,3-trichloride (XVI) with an equivalent of sodium carbonate solution. It is less aldehydic than the simpler halohydrins discussed earlier, but resembles them in some of its properties. It reduces Fehling's solution when warmed for some time; it

forms the same dinitrophenylosazone, m.p. 242°, but does not form an intermediate hydrazone. When dissolved in warm alcohol, it can be titrated with aqueous sodium hydroxide solution and neutralizes two equivalents of the base. In this reaction the 3,3-dichlorotetrahydropyran-2-ol loses its entire halogen content.



When 2,3,3-trichlorotetrahydropyran (XVI) is warmed and stirred with 3 moles of aqueous sodium hydroxide solution, the organic layer gradually disappears and the alkali is neutralized. A dark red reaction mixture results. The organic product can be isolated by evaporating the water and extracting the residue with alcohol. A quantitative yield of sodium chloride is left behind. On evaporation of the alcohol a viscous dark red halogen-free sirup is left. This material is thought to contain an equilibrium mixture of tetrahydropyranone-3-ol-2 (XVIII) and α-keto-δ-hydroxyvaleric aldehyde (XIX), together with more complex substances. It is aldehydic, reducing Fehling's solution rapidly when warmed. With 2,4-dinitrophenylhydrazine it gives, near room temperature, an almost immediate precipitate of the expected 2,4-dinitrophenylosazone (XX), m.p. 242°. On oxidation with potassium permanganate, both in alkaline and acid solution, succinic acid (XXII) has been obtained. Intermediate compounds such as α-ketoglutaric acid (XXI) have not been isolated as yet from the above oxidations or with milder oxidizing agents.

EXPERIMENTAL

Derivatives of 3-Halotetrahydropyran-2-ols

Both 3-chloro- and 3-bromo-tetrahydropyran-2-ol were prepared by the hydrolysis of the corresponding dihalides with aqueous sodium carbonate solution, following the directions of Hawkins and Bennett (2) for the preparation of 3-chlorotetrahydropyran-2-ol. The methods used for the preparation of the derivatives listed below were essentially those described by Shriner and Fuson (15).

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(*a*) *2,4-Dinitrophenylhydrazones*

The 3-chloro- and 3-bromo-tetrahydropyran-2-ol were treated at room temperature with 2,4-dinitrophenylhydrazine reagent. Voluminous orange-yellow precipitates were formed. Qualitative tests showed no halogen in the products. After repeated crystallization from absolute ethanol both products were obtained as yellow needles which melted at 133–134°C. There was no depression of the melting point when the two products were mixed.

(*b*) *2,4-Dinitrophenylosazones*

The 3-halotetrahydropyran-2-ols were refluxed with excess 2,4-dinitrophenylhydrazine in aqueous alcohol, in the presence of a few drops of concentrated hydrochloric acid. An orange-red precipitate formed in each case. On recrystallization from acetone or nitromethane orange needles were obtained which in both cases melted at 242°C. The mixed melting point indicated that the products from the two halotetrahydropyranols were the same.

(*c*) *p-Nitrophenylhydrazones*

The 3-halotetrahydropyranols were warmed for a few minutes with an alcoholic solution of *p*-nitrophenylhydrazine and a trace of acetic acid. The orange-red precipitates were halogen-free. Several recrystallizations from absolute methanol gave the same orange yellow needles which melted at 146°C.

(*d*) *p-Nitrophenylosazone*

This can be produced by prolonged heating (four hours) with excess *p*-nitrophenylhydrazine and a little concentrated hydrochloric acid. A dark red powder separated on cooling. On recrystallization from methanol it separated as fine dark red crystals which melted at 246°C. with slight decomposition.

(*e*) *Benzylphenylhydrazone*

The 3-halotetrahydropyran-2-ol in water (1 gm. in 7 ml.) was treated with benzylphenylhydrazine hydrochloride in 95% ethanol (1 gm. in 10 ml.). The mixture was warmed for a few minutes. On cooling a yellowish white precipitate formed. It was recrystallized from methanol in almost colorless needles which melted at 74–75°C.

(*f*) *Comparison with Tetrahydrofurfural Derivatives*

The derivatives from the halotetrahydropyranols described above were compared with the corresponding derivatives from tetrahydrofurfural, prepared by D. G. Hay in these laboratories by the method of Scheibler, Sotscheck, and Friese (13). Mixed melting points and other tests proved that the above products were identical in all respects with derivatives from tetrahydrofurfural.

Tetrahydropyran-2,3-diol (VIII) and Related Compounds

3-Chlorotetrahydropyran-2-ol (13.6 gm., 0.1 mole) dissolved in water (100 ml.) was treated with sodium hydroxide solution (4 gm. in 100 ml.) and allowed to stand for three to four hours at room temperature. The solution was made just acid with a few drops of dilute hydrochloric acid and allowed to

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evaporate at 35–40°C. The residue was extracted with absolute ethanol, leaving behind a quantitative yield of sodium chloride. The alcoholic extract was allowed to evaporate at room temperature. The residue (10 gm.) was extracted several times with ether. Evaporation of the ether gave a high boiling sirup (8 gm.) which is thought to be tetrahydropyran-2,3-diol. Found: C, 51.1; H, 8.07%; Calc. for $C_5H_{10}O_3$: C, 50.9; H, 8.47%.

The same product can be obtained more conveniently in larger quantities by treating crude 2,3-dichlorotetrahydropyran, made by direct chlorination of dihydropyran, with 2 moles of sodium hydroxide and isolating the product as described above.

The product gave the previously described dinitrophenylosazone (m.p. 242°) when refluxed with 2,4-dinitrophenylhydrazine. It reduced periodic acid to iodate and formed a 3,5-dinitrobenzoate, m.p. 174°C.

When the reaction with sodium hydroxide was carried out at 100° on the water bath, very little of the organic product was soluble in ether. The high boiling sirup obtained was probably a mixture of substances of higher molecular weight than the diol. In one trial a chloroform-extracted product solidified. When recrystallized from ethanol it separated in elongated plates which melted at 101–102°C. Found: C, 59.7; H, 8.10%; Calc. for $C_{10}H_{16}O_4$: C, 60.0; H, 8.00%. The melting point and analysis indicates that this is one of the $C_{10}H_{16}O_4$ substances which Hurd and Edwards (3) obtained by heating tetrahydropyran-2,3-diol.

In another trial when excess solid sodium hydroxide was added to the chlorohydrin solution and the mixture left standing, a small quantity of very fine white powder settled out. This melted at 190°C. and could be the other $C_{10}H_{16}O_4$ substance obtained by Hurd and Edwards.

3,3-Dichlorotetrahydropyranol-2 (XVII)

2,3,3-Trichlorotetrahydropyran (9.5 gm.), prepared by the method of Hawkins and Bennett (2), was stirred with sodium carbonate solution (2.6 gm. in 100 ml. of water) at 35–40° for 10 hr. The reaction mixture was then subjected to continuous extraction with ether. After evaporation of the ether a solid recrystallized from aqueous alcohol in plates which melted at 88–89°C. The I.G. Farben chemists (6) reported 90° as the melting point of 3,3-dichlorotetrahydropyran-2-ol.

This product was less aldehydic than the halohydrins, but it did reduce Fehling's solution on warming for some time. When the product was treated at room temperature with 2,4-dinitrophenylhydrazine it did not form a dinitrophenylhydrazone, but when the reaction mixture was heated the previously described 2,4-dinitrophenylosazone (m.p. 242°C.) was precipitated.

When the dichlorotetrahydropyranol was dissolved in warm alcohol, it could be titrated slowly with aqueous sodium hydroxide solution and neutralized two equivalents of the base.

2-Hydroxytetrahydropyran-3-one (XVIII)

2,3,3-Trichlorotetrahydropyran (19 gm., 0.1 mole) was warmed to 35–40°C. so it would remain in the liquid phase, and sodium hydroxide solution (12 gm., 0.3 mole, in 150 ml. of water) was added. The mixture was kept at the

temperature indicated and stirred until the organic layer had disappeared—about 10 hr. The reaction mixture still slightly acid was then allowed to evaporate at just above room temperature. The residue was extracted with absolute ethanol, leaving behind a nearly quantitative yield (16 gm.) of sodium chloride. The alcoholic extract on evaporation gave a very viscous, dark red sirup (10 gm.). No method of purifying it has been found. Its reactions indicated that it was mainly 2-hydroxytetrahydropyran-3-one in equilibrium with an open chain aldehyde form.

It reduced Fehling's solution rapidly when warmed. With 2,4-dinitrophenylhydrazine it gave an almost immediate precipitate of the expected 2,4-dinitrophenylosazone (m.p. 242°), previously described.

The crude red sirup was treated at room temperature for several days with an alkaline solution of potassium permanganate. The manganese dioxide was filtered off and the filtrate acidified with dilute sulphuric acid. Further decolorization of the permanganate now occurred. When this acid oxidation was complete the excess permanganate was destroyed with a little sodium bisulphite, the solution evaporated to dryness, and the residue extracted with ether. On evaporation of the ether a solid acid (m.p. 186°) was left. This was identified as succinic acid by the preparation of the *p*-bromophenacyl ester (m.p. 210–211°) and the *p*-nitrobenzyl ester (m.p. 87–88°). Mixed melting points of these derivatives with samples prepared from an authentic specimen of succinic acid showed no depression.

ACKNOWLEDGMENTS

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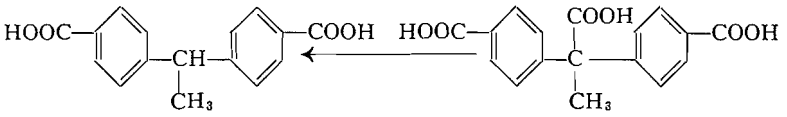
SYNTHESIS OF 1,1-DI-(*p*-CARBOXYPHENYL)ETHANE AND ITS ESTERS[1]

By Henry Bader[2] and W. A. Edmiston

ABSTRACT

The condensation of chlorobenzene with ethylidene diacetate in presence of fluosulphonic acid – hydrogen fluoride catalyst has been improved to give high yields of 1,1-di-(*p*-chlorophenyl)ethane, which was converted into the corresponding dinitrile by a modification of the cuprous cyanide method. Alkaline hydrolysis of the dinitrile gave 1,1-di-(*p*-carboxyphenyl)ethane. Its methyl and 2-ethylhexyl esters were prepared directly from the diacid or via the diacid chloride.

The interesting properties of the polyesters of terephthalic acid prompted us to prepare other aromatic *p*-diacids expected to possess similar properties, i.e. 1,1-di-(*p*-carboxyphenyl)ethane (I).



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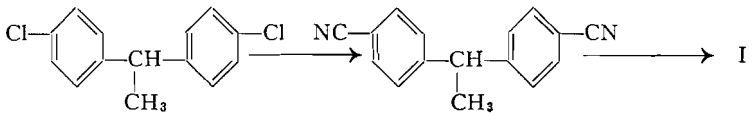
This compound was previously obtained by Haiss (4) by partial decarboxylation of 2,2-di-(*p*-carboxyphenyl)propionic acid (II), which was produced by oxidation of the condensation product of toluene and pyruvic acid.

The simplest approach to the synthesis of compound (I) would be to oxidize 1,1-di-(*p*-tolyl)ethane to the diacid or to the dialdehyde, as described by Perron and Barré (8, 9) for the 2,2,2-trichloro-1,1-di-(*p*-tolyl)ethane. However, the stability of the ethylidene bridge is much lower than that of the trichloroethylidene group and it is the first one attacked on oxidizing 1,1-di-(*p*-tolyl)-ethane. Thus Anschütz (1) reported formation of di-*p*-tolyl ketone and of *p*-toluylbenzoic acid when hot chromic acid was used, and similarly in this laboratory (5) chromium trioxide in glacial acetic acid at 55° gave only di-*p*-tolyl ketone.

This synthesis was carried out successfully through the route outlined in the following scheme:



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[1]*Manuscript received November 14, 1955.*
Contribution from the Research Laboratory, Dominion Tar and Chemical Company Limited, Ville LaSalle, Quebec.
[2]*Present address: Ortho Research Foundation, Raritan, N.J., U.S.A.*

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The starting material, 1,1-di-(*p*-chlorophenyl)ethane, was prepared by an improvement of the method previously evolved in this laboratory (2). The original method gives a 48.6% yield of the isomeric mixture of 1,1-di-(chlorophenyl)ethane by reacting chlorobenzene with ethylidene diacetate in presence of a mixture of fluosulphonic acid and hydrogen fluoride. It has now been found that the presence of sulphuric acid in the reaction mixture lowers the yield of the product. When the fluosulphonic acid is redistilled immediately before use and thus freed from the sulphuric acid it contains, the yield of mixed isomers can be raised to 71.5%. The solid *p,p'* isomer can be easily isolated and purified by crystallization.

When the conversion of the dichloride (III) into the dicyanide (IV) was attempted with cuprous cyanide in pyridine or quinoline under the standard conditions described in the literature (cf. *inter alia* Newman (7)), there resulted an extensive charring of the product and the reaction was incomplete, the monochlorocyanide being the main product. By using, however, at least a three times higher molar ratio of the organic base to cuprous cyanide than is customary, a good yield of 1,1-di-(*p*-cyanophenyl)ethane (IV) was obtained. While our work was in progress Lorz and Baltzly (6) reported improved yields of 4-alkoxy-1-naphthonitriles by doubling the amount of pyridine used by Newman (7) thus confirming our findings.

The dinitrile was hydrolyzed to the corresponding diacid (I) in almost theoretical yield by alkaline hydrolysis in the presence of glycol. Ethanol, propanol, or glycerol can also be used, the time of the reaction depending on the boiling point of the alcoholic component.

Some attempts were made to synthesize the diacid (I) or its esters by a one stage process from benzoic acid or methyl benzoate using ethylidene chloride, ethylidene diacetate, or acetaldehyde in presence of sulphuric acid, aluminum chloride, fluosulphonic acid, hydrogen fluoride, or the fluosulphonic acid – hydrogen fluoride mixture. Also condensations of acetylene in presence of aluminum chloride or mercuric chloride were tried, but no reaction took place under any of these conditions.

The dimethyl ester of the diacid (I) was best prepared by converting the diacid to its dichloride with thionyl chloride and treating the dichloride with methanol. The di-2-ethylhexyl ester was prepared directly from the diacid and 2-ethylhexanol in presence of sulphuric acid and of xylene as an azeotropic component.

EXPERIMENTAL*†

1,1-Di-(p-chlorophenyl)ethane

Chlorobenzene (1410 gm.) was charged to a stainless steel reaction vessel and cooled to 0°. Under vigorous stirring 1000 gm. of liquid hydrogen fluoride were first added, followed by 1675 gm. of freshly redistilled fluosulphonic acid, and then a mixture of ethylidene diacetate (490 gm.) and of chlorobenzene (770 gm.) was introduced dropwise over a period of 40 min. while the tempera-

All melting points are uncorrected.
†*The microanalyses were performed by Dr. Robert Dietrich of Zurich, Switzerland.*

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ture rose slowly from 0° to 20°. The temperature was maintained at about 10° while the reaction mixture was agitated for another 30 min. It was then poured into 6 liters of ice water, the organic layer separated after the addition of some ether, and then washed with dilute caustic and water. After removal of the solvent the residue was fractionally distilled, yielding recovered chlorobenzene (1650 gm.) and 1,1-di-(chlorophenyl)ethane (603 gm.; 71.5% yield based on ethylidene diacetate) as a pale yellow oil, boiling point 138–142° at 1.0 mm.; refractive index, n_D^{21} 1.5920. The major portion of the product crystallized on standing a few hours at room temperature. The supernatant liquor was decanted and the solid crystallized from methanol yielding 1,1-di-(*p*-chlorophenyl)ethane (375 gm.; 56.8% over-all yield) as colorless prisms melting at 53–55° (Grummit *et al.* (3) give m.p. 54–55°).

1,1-Di-(p-cyanophenyl)ethane

A mixture of 1,1-di-(*p*-chlorophenyl)ethane (475 gm.), cuprous cyanide (415 gm.; dried before use for 36 hr. at 110°), and anhydrous quinoline (1200 ml.; distilled over potassium hydroxide) was refluxed for 70 hr., then poured while still hot into a solution of ammonium hydroxide (1800 ml.; d. = 0.88) and water (1800 ml.). Benzene (1600 ml.) was added, the mixture allowed to cool to room temperature, and then ether (1000 ml.) was added. A brown solid separated which was removed by filtration. The organic layer was washed with dilute ammonia solution (4 × 1200 ml.), with a hydrochloric acid solution (2 *N*; 2 × 1200 ml.; a precipitate which separated at this stage was removed by filtration), then with water (2 × 1200 ml.) and finally with saturated brine (2 × 1200 ml.). The solution was dried over anhydrous copper sulphate and the solvent removed by distillation yielding the crude dinitrile (312 gm.; 71% yield). Crystallization from ethanol gave 1,1-di-(*p*-cyanophenyl)ethane (249 gm.) as colorless prisms which had a melting point of 112–118°C. After one more crystallization, the melting point was increased to 120–122.5°. Calc. for $C_{16}H_{12}N_2$: C, 82.75; H, 5.2; N, 12.05. Found: C, 82.65; H, 5.05; N, 12.3.

1,1-Di-(p-carboxyphenyl)ethane

A mixture of 1,1-di-(*p*-cyanophenyl)ethane (216 gm.), sodium hydroxide (120 gm.), ethylene glycol (1200 ml.), and water (240 ml.) was refluxed for 10 hr. by which time evolution of ammonia ceased. After it was cooled to room temperature, the solution was separated from a small amount of solidified oily material, diluted with ice water, and acidified with dilute hydrochloric acid under vigorous stirring. The resulting precipitate was filtered under suction, washed several times with water, and brought to a consistency of a cake by applying suction for several hours. The latter was dried either in an oven at 110° or by azeotropic distillation with benzene or xylene. In this way 1,1-di-(*p*-carboxyphenyl)ethane (239 gm.; 95.1% yield) was obtained in microcrystals, which melted at 265–278°, and then, on crystallization from ethyl acetate, at 273–278°. Calc. for $C_{16}H_{14}O_4$: C, 71.1; H, 5.2. Found: C, 71.7; H, 5.2.

1,1-Di-(p-carboxyphenyl)ethane Dimethyl Ester

Thionyl chloride (150 ml.) was added slowly to the diacid (150 gm.) causing heat evolution and progressive dissolution of the solid. The mixture was refluxed for one hour, then the excess of thionyl chloride removed under reduced pressure. To the residue methanol (150 ml.) was slowly added and then the mixture refluxed for a period of one hour and the excess methanol distilled off. The residue was taken up in ether, washed twice with sodium carbonate solution and then with water, and finally dried over anhydrous magnesium carbonate. Evaporation of the solvent left 1,1-di-(*p*-carbomethoxyphenyl)-ethane (156.9 gm.; yield 94.3%) which crystallized on standing. Recrystallization from cyclohexane–ether mixture or from ether gave colorless plates which melted at 56.5–58.2°. Calc. for $C_{18}H_{18}O_4$: C, 72.5; H, 6.1. Found: C, 72.35; H, 5.95.

1,1-Di-(p-carboxyphenyl)ethane Di-(2′-ethyl)hexyl Ester

A mixture of 1,1-di-(*p*-carboxyphenyl)ethane (355.4 gm.), 2-ethylhexanol (2000 ml.), concentrated sulphuric acid (55 gm.), and dry xylene (500 ml.) was refluxed for 100 hr. while water was separated in a Dean and Stark trap. The resulting solution was then washed with sodium carbonate solution and the excess of xylene and alcohol was distilled. Fractionation of the residue under reduced pressure gave 1,1-di-(*p*-carboxyphenyl)ethane di-(2′-ethyl)-hexyl ester (496.0 gm.; yield 76%) which boiled at 220° at 0.05 mm.; refractive index, n_D^{23} 1.5252. Calc. for $C_{32}H_{46}O_4$: C, 77.7; H, 9.4. Found: C, 77.45; H, 9.05.

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CROSS-LINKING OF COPOLYMERS FROM METHYL VINYL KETONE AND *n*-BUTYL ACRYLATE[1]

By W. Cooper and E. Catterall

ABSTRACT

Copolymers of *n*-butyl acrylate and methyl vinyl ketone can be cross-linked by a combination of sulphur and zinc oxide; the reaction is associated with the methyl vinyl ketone units in the polymer chain. From studies on the copolymers and model compounds, it is suggested that adjacent pairs or groups of methyl vinyl ketone units in the polymer cyclize to give $\alpha\beta$ unsaturated ketone groups. These contain reactive hydrogen which is attacked by sulphur; disulphide or zinc mercaptide cross-links are then formed. Water is produced in the cyclization reaction and hydrolyzes some of the ester groups; additional cross-links are thus formed by reaction of the acid groups with zinc oxide. The ease of cyclization and, therefore, the extent of cross-linking is dependent on the method of preparing the copolymers, emulsion copolymers being much more reactive than those prepared in solution. A comparison has been made between the sulphur + zinc oxide system and other cross-linking agents which may be used for polyacrylates.

INTRODUCTION

The elastomeric polymers and copolymers of acrylic esters are of growing importance and have attracted much attention in recent years. Some of the lower polyalkyl acrylates are attractive rubbers of reasonable strength with good resistance to heat and oils. Polymers containing high proportions of *n*-butyl acrylate possess in addition good resistance to freezing and high resilience. They are, however, usually difficult to process and give products of low strength. Efforts to improve these features have been made by copolymerization with a more polar type of monomer, such as acrylonitrile, methyl *iso*propenyl ketone, and methyl vinyl ketone, though with some sacrifice of other desirable properties.

The copolymers of *n*-butyl acrylate with methyl vinyl ketone are of some interest in that they can be cross-linked by means of sulphur + zinc oxide in addition to the more usual cross-linking agents (11) (such as lead oxide, calcium hydroxide, or polyamines), and give products of good strength when reinforced by means of carbon black or finely divided silica (4).

A preliminary study of the reactions involved indicated that they were rather complex and this paper describes the attempts made to elucidate those of greater importance and, as a practical measure, to compare the sulphur + zinc oxide vulcanizates with those prepared with other cross-linking agents.

DISCUSSION

Polymer

Methyl vinyl ketone and *n*-butyl acrylate copolymerize readily, the polymers containing a higher proportion of methyl vinyl ketone than in the initial monomer. Determination of the composition of low conversion copolymers for

[1]*Manuscript received October 24, 1955.*
Contribution from the Chemical Research Division, Dunlop Research Centre, Birmingham, England. This paper was read at the Sixth Canadian High Polymer Forum at St. Catharines, Ontario, April 14th, 1955.

monomer reactivity ratios proved to be difficult (see Appendix for details), and a completely satisfactory method has not been found. Reasonable agreement was found, however, between several methods of analysis, and values of $r_1 = 1.6 \pm 0.1$ and $r_2 = 0.65 \pm 0.07$ were obtained (MVK is monomer 1). The data are shown in the polymer composition curve (Fig. 1).

Integral and differential copolymer distribution diagrams (13) (Figs. 2*a* (i) and (ii) and 2*b* (i) and (ii)) show that, up to about 50% conversion, copolymers made with 20–35% by weight of methyl vinyl ketone (i.e. 30–50 mole %) have only a narrow distribution of polymer compositions. The copolymers were made by solution polymerization and in emulsion. Solution polymers were prepared in benzene solution at 70° using 0.5% benzoyl peroxide as catalyst and isolated by pouring into petroleum ether, or aqueous alcohol mixtures. They were normally of relatively low molecular weight ($[\eta] = 0.2$–0.3) and completely soluble in organic solvents. The emulsion copolymers were made at 50° using potassium persulphate (1% on monomers) as initiator. For copolymers of low methyl vinyl ketone content, the sodium salt of sulphated methyl oleate (4.2%) was used as the emulsifier, while for high ketone contents sodium lauryl sulphate (4%) was more suitable. The emulsion copolymers were

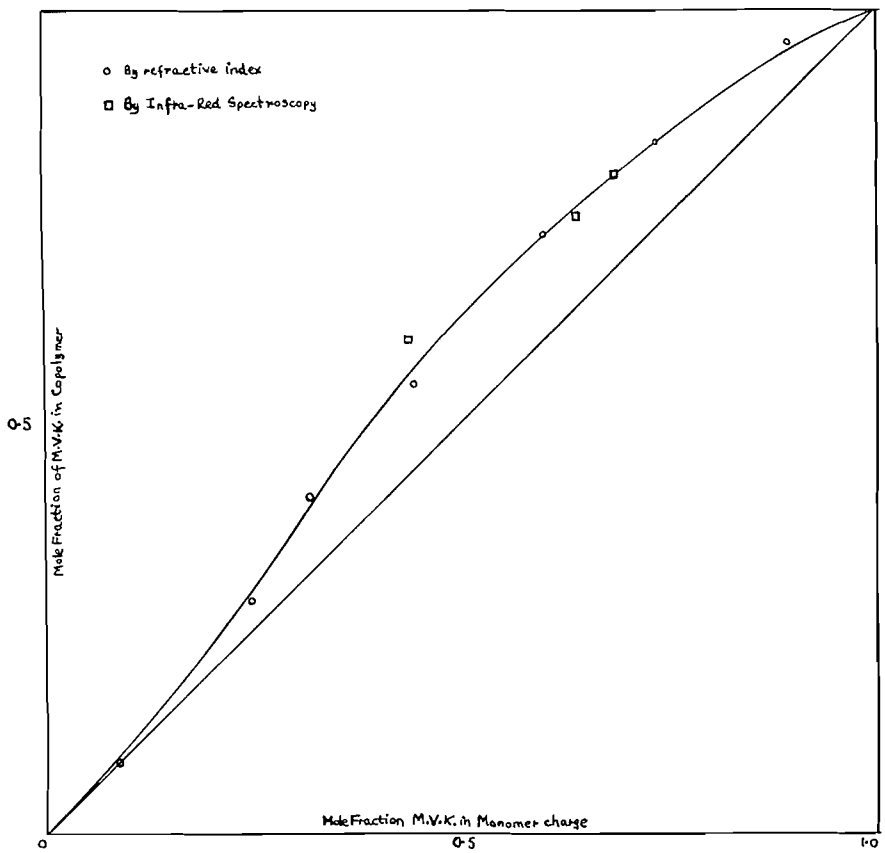

FIG. 1.

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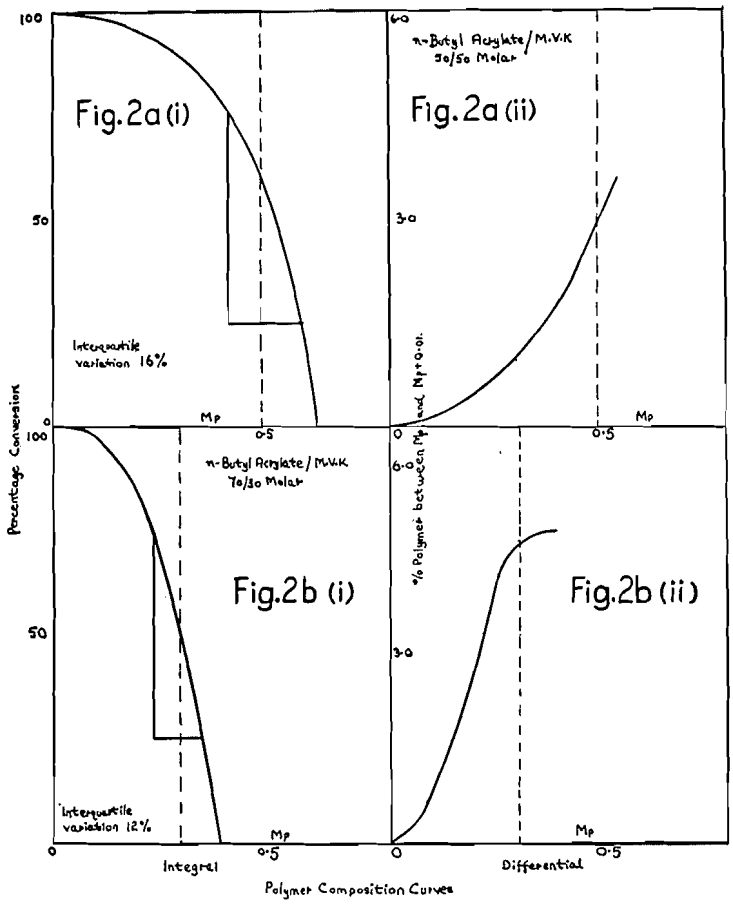

FIG. 2.

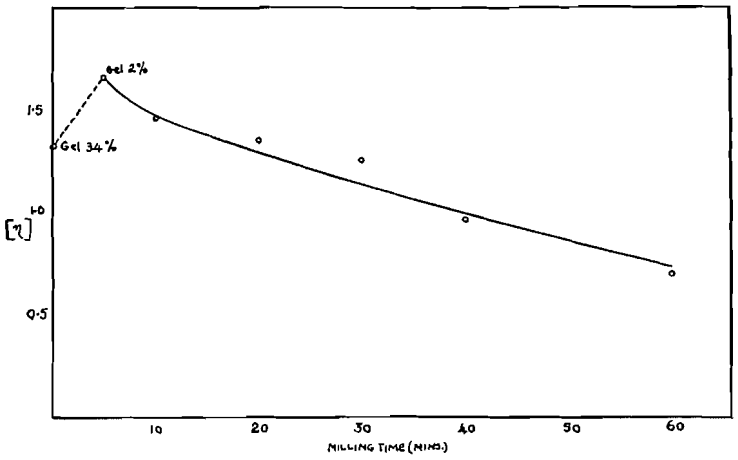

FIG. 3.

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always gelled to a greater or lesser extent. This gel was broken down readily on milling, and, as with other acrylates (6), there was a steady fall in molecular weight with mastication (Fig. 3).

Cross-Linking Agents for Acrylate Copolymers

A variety of reagents have been used for cross-linking acrylate copolymers. Most of them attack the ester portions of the molecule and thus apply to all types, but some (e.g. hexamethylene tetramine (HMT) for copolymers with alkyl vinyl ketones) are more specific in their action. The more important substances used include the following:

(*a*) *Basic oxides and hydroxides* (e.g. lead oxide and calcium hydroxide) which form salt bridges between different chains (i). It has been suggested

$$\underset{\text{(i)}}{\{\text{—C(O)OMOC(O)—}\}} \qquad \underset{\text{(ii)}}{\{\text{—CO—}\}\text{—COOR}}$$

that strong bases from monovalent metals (e.g. KOH) may form cross-links by an acetoacetic ester type condensation (ii) (12). This has not been proved, however, and will be discussed later.

(*b*) *Polyamines.*—These presumably form amide bridges between the polymer chains (iii). Substances such as tetraethylenepentamine (TEP) and triethyl trimethylene triamine (Trimene Base) are the most commonly used.

$$\underset{\text{(iii)}}{\{\text{—CONH—R—NHCO—}\}} \qquad \underset{\text{etc.}}{R = [(CH_2)_2NH(CH_2)_2]_n}$$

(*c*) *Peroxides.*—Peroxides are used occasionally to effect cross-linking of polyacrylates. Abstraction of hydrogen atoms (probably skeletal hydrogen atoms adjacent to the carbonyl group) followed by dimerization of the radicals so formed is probably their mode of action. They are generally not very useful materials and tend to cause blowing.

(*d*) *Sulphur + zinc oxide.*—Pure polyacrylates will not cross-link with these reagents. The possession of halogen atoms, by incorporation, for example, of chloroethyl vinyl ether, or the presence of ketone groups renders them effective. This reaction is discussed in detail below.

(*e*) *Miscellaneous compounds.*—These include, for ketone copolymers, hydrazine (used as its organic salts in the presence of a base) which forms intermolecular azines (iv), hexamethylene tetramine + organic acids or paraformaldehyde which form interchain methylene bridges (v), trinitrobenzene + zinc oxide, and quinone dioxime + lead oxide. The mechanism by which the latter compounds react is not known.

$$\underset{\text{(iv)}}{\left\{ \begin{array}{l} \text{—C=N—N=C—} \\ \quad\;\; | \qquad\quad | \\ \quad CH_3 \qquad CH_3 \end{array} \right\}} \qquad \underset{\text{(v)}}{CH_3CO\text{—}\{\text{—}CH_2\text{—}\}\text{—}COCH_3}$$

Cross-linking by Sulphur + Zinc Oxide

Examination of vulcanizates from *n*-butyl acrylate and MVK quickly leads to the conclusion that rapid reaction occurs with sulphur and that concomitant

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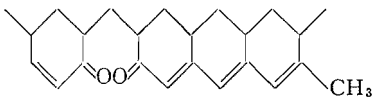
reactions associated with the polymer structure also occur. These latter reactions manifest themselves in greatly reduced heat-aging resistance of the copolymers. It is convenient, therefore, to discuss first the changes which occur on heating the copolymers alone.

(*i*) *Cyclization of MVK Polymers*

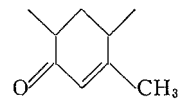
A feature of all compounded emulsion copolymers examined was a continuous and relatively large weight loss when heated above 100° C., accompanied by reduced swelling in a solvent such as benzene. This seemed to be in accordance with the view that the weight loss resulted from intermolecular condensation with consequent cross-linking and reduced swelling volume, until it was observed that weight loss – swelling volume measurements did not agree with estimates of cross-linking as judged from physical tests on cured slabs. This became further apparent when it was found that the pure gum copolymers themselves gave comparable weight loss and swelling volume curves but gave no sign of possessing a truly vulcanized structure. Furthermore, soluble copolymers (prepared by bulk or solution polymerization) when heated in the absence of air also lost weight. They became hard and resinous but, since they were completely soluble in methyl ethyl ketone and were thermoplastic, they were not cross-linked.

As a result of these observations, experiments were made on a solution copolymer containing 50–60% of MVK. (Initial monomer composition equimolar; for copolymer distribution curve see Fig. 2*a*.) On heating for 93 hr. at 160° C. in a sealed evacuated vessel, 5.1% of butanol and 4.0% of water were liberated. The polymer was transformed from a soft rubber to a hard resin, had a deep red-brown color, and was soluble in chloroform or methyl ethyl ketone. Titration showed the presence of 3.2% acid groups (calculated as acrylic acid).

Marvel and Levesque (10) studied the change in polymethyl vinyl ketone when heated at 270–360° C., and deduced the formation of polycyclic structures of the type (vi).



(vi)



(vii)

Infrared spectroscopic examination of the heated copolymer showed changes which were quite consistent with this type of structure (Fig. 4). Reduction of the intensities of the normal ketone absorption frequency and other associated bands was accompanied by new frequencies characteristic of $\alpha\beta$ unsaturated ketones; the ester carbonyl group remained essentially unchanged. It is clear therefore that reactions of the type described by Marvel occur quite rapidly at temperatures as low as 140°–160° C.[2] Calculation of the extent of this reaction by use of Wall's statistical theory for the isolation of carbonyl groups (15) in the copolymer shows that 6.1% of water would be eliminated;

[2]*The ultraviolet spectra of the copolymers were rather featureless, but an appreciable increase in absorption intensity, particularly at higher frequencies, occurred after only 30 min. at 140° C.*

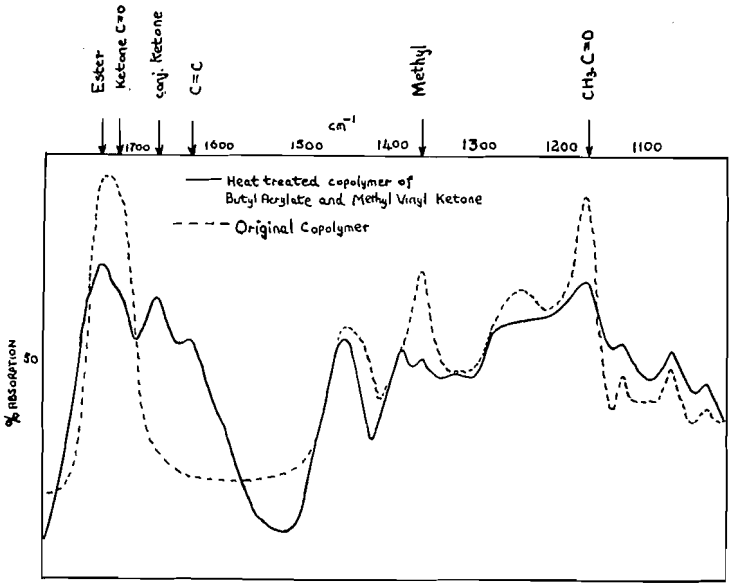


FIG. 4.

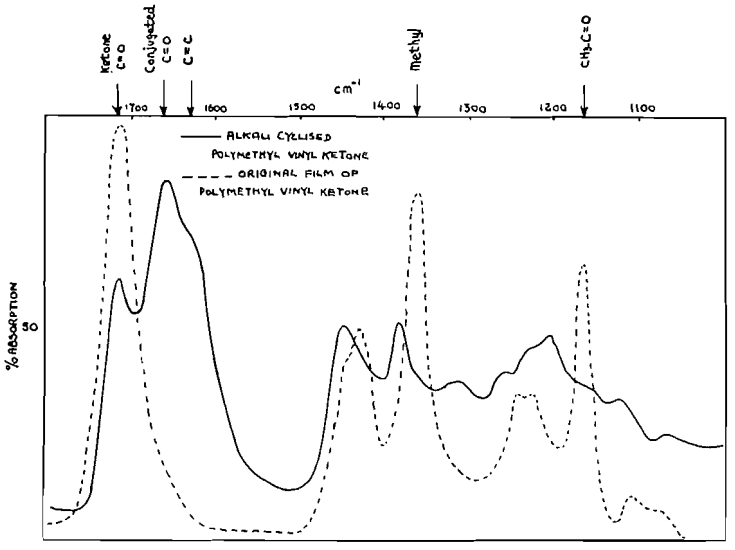


FIG. 5.

about two thirds of the residual carbonyl groups would be conjugated with ethylenic bonds. On the assumption that the monomer units were randomly distributed in the copolymer the experimental data show the reaction to have gone to about 80–85% completion.[3] This estimate is in agreement with the intensity changes of bands in the infrared spectrum of the copolymer corresponding to carbonyl and methyl groups.

[3]*The r_1, r_2 product for this system is not greatly different from unity; it follows that errors brought about by this assumption will not be great.*

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This condensation proceeds very slowly at temperatures below 100° C., but it has been found that polymethyl vinyl ketone and its copolymers rapidly give polyunsaturated ketones at room temperature on treatment with alkali. (Polymethyl vinyl ketone is transformed in a few seconds from a tough thermoplastic resin softening at about 50° C. to a hard brittle resin softening at 260–270° C. (5).) Under these conditions not a great deal of multiple ring closure occurs and mono-ring structures predominate (vii) (the infrared spectrum of the alkali cyclized polymer is shown in Fig. 5) and, as insoluble polymers are easily obtained, it is possible for some intermolecular condensation also to occur. It is obvious then that polymers containing methyl vinyl ketone can undergo rapid condensation reactions at room temperature in the presence of alkalies, or alone at vulcanization or heat aging temperatures. A further consequence of the cyclization reaction is the formation of carboxyl groups by hydrolysis of ester groups. In the presence of metallic oxides or hydroxides, this will result in many cross-links being formed.

The combined effect of these reactions undoubtedly results in continued cross-linking on heating and thus poor heat aging resistance. Confirmation of these views is found in the large amount of butanol liberated on heating a copolymer with lead oxide compared with that from pure poly *n*-butyl acrylate under the same conditions (Table I).

TABLE I

Polymer*	% Butanol	% Water	% Swelling volume in benzene
100% Butyl acrylate	1.27	0.08	1050
70 BA/30 MVK	7.44	0.66	150

**Heated at 140° C. in vacuo for 10 hr.*

(ii) Reaction of Sulphur with Acrylate–MVK Copolymers

Hydrogen sulphide is evolved when a polymer containing methyl vinyl ketone is heated with sulphur, and some sulphur becomes combined with the polymer. Zinc oxide when present reacts with the hydrogen sulphide to give zinc sulphide. The amounts of sulphur combined and that liberated as hydrogen sulphide have been determined and the results are shown in Table II. It was found that approximately twice the amount of sulphur remained combined

TABLE II

Polymer	Curing system	% Swelling* volume	% Eliminated		% Sulphur			
			H_2O	*n*-BuOH	Init.	H_2S	Combined	Free
100 BA†	2% S, 10% ZnO	Dissolved	0.01	0.35	2.00	—	—	2.00
70 BA/30 MVK	2% S, 10% ZnO	760	1.08	1.28	1.98	0.57	0.87‡	Neg.
	4% S	2210	0.71	0.45	3.97	0.44	0.94‡	2.40

**Benzene.*
†BA = n-butyl acrylate.
‡Some sulphur was also present in odorous low molecular weight material extractable by benzene.

with the copolymer compared with that liberated as hydrogen sulphide, and that the reaction was substantially complete in about one hour; little hydrogen sulphide was liberated after this period.

As would be expected the amount of hydrogen sulphide evolved depended on the amount of MVK in the copolymer. This was determined for a number of high and low conversion copolymers and the results are summarized in Fig. 6.

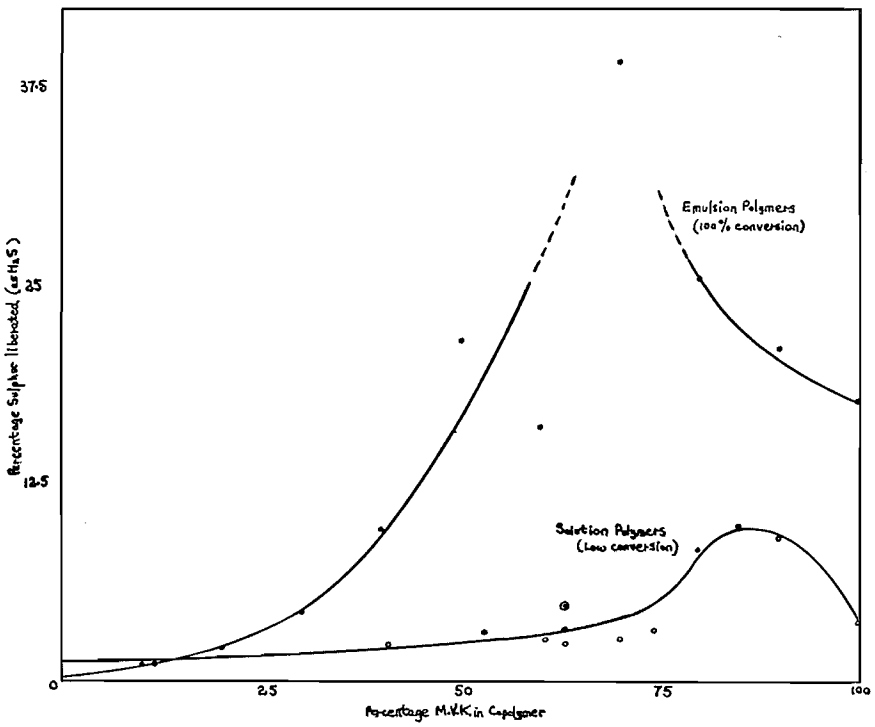

FIG. 6.

Two features are at once apparent, firstly that emulsion copolymers liberate much more hydrogen sulphide than those prepared in solution, and secondly that there is a maximum in the curve relating the amount of hydrogen sulphide liberated to the MVK content of the copolymer. With regard to the differences between emulsion and solution copolymers, it seemed possible that these may have arisen because of the different methods employed in incorporating the sulphur into the copolymers; in the case of emulsion polymers it was mixed on the mill while with solution polymers sulphur and polymer were dissolved in benzene and the solvent removed under vacuum. To test this point two 50/50 w/w copolymers were made, one in emulsion, the other in solution; both were taken to about 60% conversion. Sulphur (4%) was incorporated into both by milling and by use of a solvent. The hydrogen sulphide liberated on heating is given in Table III, together with the yields of volatiles liberated on heating the polymers alone at 150° C. It is apparent that a more intimate mixture of

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TABLE III

Copolymer	% S liberated as H_2S*		Volatiles liberated on heating†	
	(*a*) Milled	(*b*) In solution	% H_2O	% Butanol
Emulsion	0.21	0.54	2.5	0.7
Solution	0.02	0.04	*ca.* 0.05	*ca.* 0.05

**Heating at 150° C. for three hours.*
†At 150° C. for eight hours.

polymer and sulphur is obtained by the solution technique and that under both conditions the emulsion copolymer liberates much more hydrogen sulphide. This is accompanied by the ready loss of water, undoubtedly from cyclization, on heating. (Evidence to support the view that cyclization to give an $\alpha\beta$ unsaturated ketone is a prerequisite for attack by sulphur is presented below.) The reason for the susceptibility of emulsion copolymers to this reaction is not fully understood since spectroscopic examination of the unheated emulsion copolymer shows no evidence of prior cyclization. It follows that either the emulsion copolymers have different compositions (MVK is a water miscible monomer) or traces of reagents from the emulsion system accelerate the cyclization. The latter is the more probable, as no evidence of heterogeneity was observed on fractionating an emulsion copolymer from the latex. Furthermore the refractive indices of emulsion copolymers containing 70% or more of butyl acrylate were the same as those of the corresponding solution copolymers. Mixtures of the two homopolymers were not homogeneous and gave refractive index values substantially the same as polybutyl acrylate, irrespective of composition.

The explanation for the maxima in the curves relating the hydrogen sulphide liberated vs. polymer composition is even less obvious. The most probable cause is a reduction in solubility of sulphur in the higher ketone copolymers, particularly after some cyclization has occurred. It is also possible that a change occurs in the ratio of sulphur eliminated as hydrogen sulphide to that which combines with polymer.

That the attack of sulphur on the copolymers is a free radical reaction is shown by the fact that the rate of liberation of hydrogen sulphide is increased by the addition of the conventional rubber accelerators (MBT, TMD) as shown in Fig. 8. A study of the change in modulus of the polymer with heating time (Fig. 7) shows clearly the influence of accelerator on the rate of cure.

In these systems zinc oxide has the effect of taking up hydrogen sulphide, which causes blowing and some reversion by reducing disulphide cross-links, reacts with acid groups formed by hydrolysis of the ester (separate experiments on the pure polyacrylates showed zinc oxide alone to have a negligible cross-linking effect), and forms mercaptide cross-links by the reaction with thiol groups along the polymer chain.

The above experiments show conclusively that sulphur reacts with MVK polymers and copolymers, and that cyclization with loss of water also occurs. The latter can be a major reaction and its effect, particularly in the presence of metallic oxides, can completely mask the influence of the sulphur.

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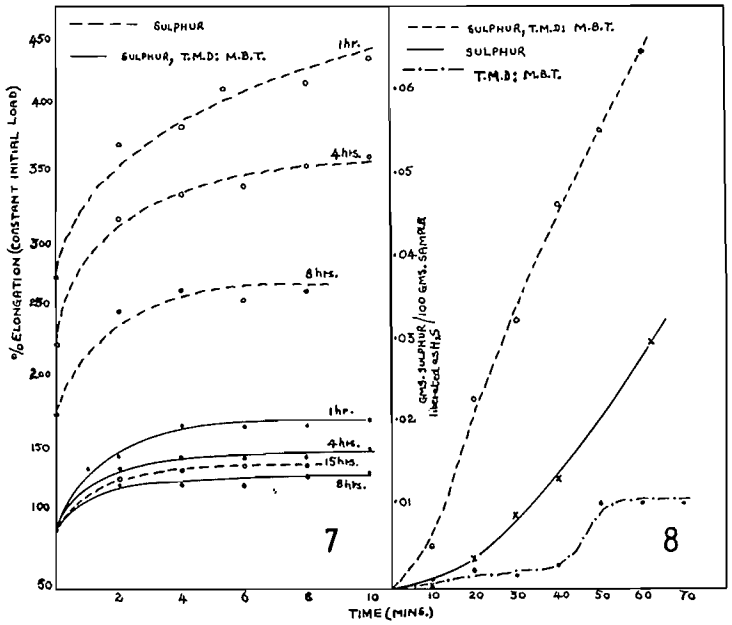
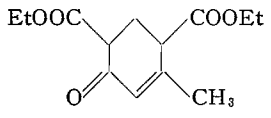


FIGS. 7 AND 8.

(iii) Mechanism of Sulphur–Copolymer Reaction

In order to decide the nature of the reaction a number of model compounds were heated with sulphur at 150° C. and the hydrogen sulphide evolution observed. The results are summarized in Table IV and show that the reaction of sulphur with ketones is not a general reaction. Stable aliphatic ketones do not react at the temperatures used in vulcanization of the copolymers, and it is interesting to note that those saturated ketones which do react possess two carbonyl groups in close proximity (e.g. acetyl acetone, dimethyl dihydroresorcinol), or can undergo condensation to give an unsaturated ketone. Thus cyclohexanone gives 2-(cyclohex-1′-enyl) cyclohexanone, 1,3-diacetyl diethyl glutarate can give 4,6-dicarboethoxy-3-methyl cyclohex-2-enone (viii), and, as already discussed, polymethyl vinyl ketone gives a cyclized polymer (v) on heating.



(viii)

It appears that not all unsaturated ketones liberate hydrogen sulphide under these conditions, as shown by the cases of mesityl oxide and its higher homologue 5-methyl-4-hexen-3-one, which differ from the other unsaturated ketones examined in that they do not possess a secondary or tertiary hydrogen atom adjacent to the double bond. It follows from the behavior of 5-methyl-4-

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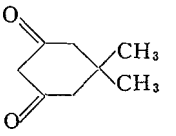
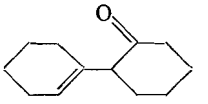
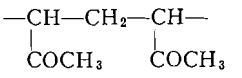
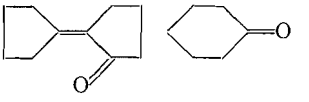
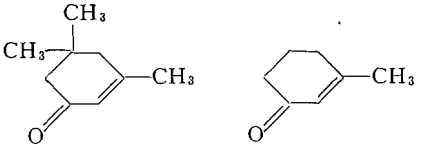
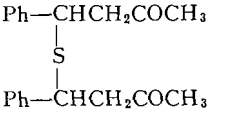
TABLE IV*

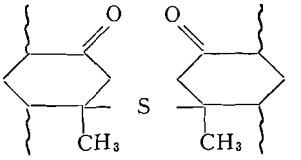
Hydrogen sulphide not liberated	Hydrogen sulphide liberated	
CH_3COCH_3	$CH_3COCH_2COCH_3$	++++
$CH_3COCH(CH_3)_2$		+++
$CH_3COCH_2CH(CH_3)_2$		
	$CH_3CO(CH_2)_2COCH_3$	+
$CH_3COCH(CH_3)CH_2CH_3$		
$CH_3CO(CH_2)_3COOC_4H_9$	$(CH_3COCH(COOEt))_2CH_2$	+
$CH_3COCH{=}C(CH_3)_2$		++
$CH_3CH_2COCH{=}C(CH_3)_2$		+++
		+++
		++

The ketones were heated at 150° C. for periods of 10–20 hr. In the case of those which liberated H_2S the speed of reaction is indicated by the + signs.

hexen-3-one, as with the saturated ketones, that the possession of a secondary hydrogen atom adjacent to the carbonyl group does not lead to the formation of hydrogen sulphide (unless of course it is instantly removed by rapid addition to the double bond—an unlikely possibility[4]).

[4]*Hydrogen sulphide reacts readily with αβ unsaturated ketones. Benzal acetone for example gives (xi) (2), and a comparable reaction with cyclized MVK would form (xii). This type of*

(xi) 

(xii) 

reaction seems sterically improbable however, in view of the ring structure elements and, of course, the ready evolution of hydrogen sulphide in the reaction is evidence against it.

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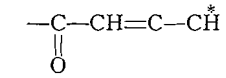
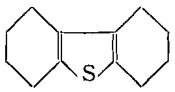
It seems therefore that the following structure grouping is necessary, ab-

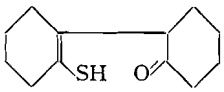


straction of hydrogen by sulphur occurring at the point marked by an asterisk.

The behavior of 2(cyclohex-1′-enyl) cyclohexanone is apparently anomalous, but it must be remembered that in this case the $\beta\gamma$ system is more than usually reactive.[5] This compound when heated with sulphur forms 1,2,3,4,6,7,8,9-octahydrodibenzothiophen (ix), in good yield (3). The formation of this compound, however, is not directly relevant to the reaction in question. It can be



(ix)



(x)

obtained directly from 2(cyclohex-1′-enyl) cyclohexanone (3) by addition of sulphur and loss of water, without any necessity of explaining the ready formation of hydrogen sulphide. A possible intermediate in the formation of (ix)

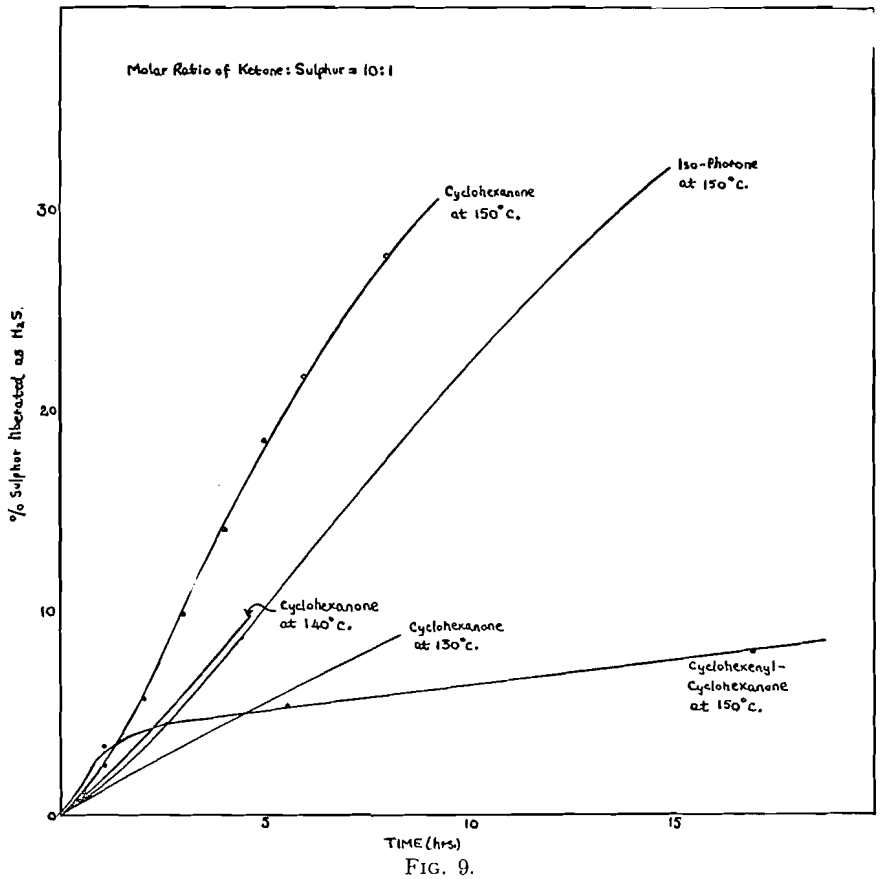


FIG. 9.

[5]*This is apparent from its formation from cyclohexanone on heating instead of 2-cyclohexylidene cyclohexanone.*

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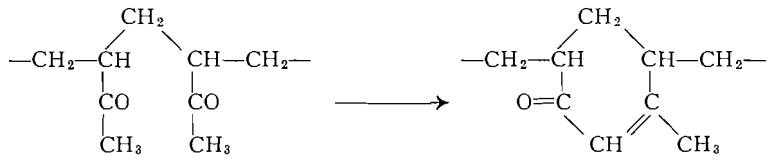
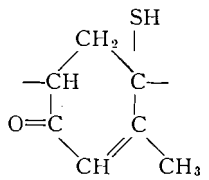
would be the thiol (x). Hydrogen sulphide, on the other hand, would be liberated after attack on the hydrogen atoms alpha to the double bond (positions 2′, 6′, or 1) giving complex sulphides (7). It is probable that such reactions may also occur since hydrogen sulphide is evolved continuously on heating (see Fig. 9) but in smaller amounts than from cyclohexanone.

The following mechanism, which is supported by the above evidence, is that, initially, cyclization occurs between adjacent pairs or groups of MVK units.



The unsaturated structures are attacked by sulphur to give structure elements (xiii).



(xiii)

Oxidation of some of the thiol groups by sulphur could then occur with the formation of disulphide bridges and the liberation of hydrogen sulphide (xiv), while others would react with zinc oxide to form mercaptide cross-links (xv).

$$2RSH + S \rightarrow RS \cdot SR + H_2S \qquad \text{(xiv)}$$

$$2RSH + ZnO \rightarrow RSZnSR + H_2O \qquad \text{(xv)}$$

It is possible that this latter reaction is of some consequence in view of the necessity of using a combination of the zinc oxide and sulphur, which separately possess only weak cross-linking action under normal cure times and temperatures. The influence of the accelerator is presumably activation of the sulphur by opening the S_8 ring (8). The fact that, ultimately, vulcanizates of comparable state are obtained with or without accelerator, and that there is then no free sulphur available, supports this view.

It may be concluded that the effect of the ketone monomer is only to provide, by condensation, unsaturated groups which can then react with sulphur.

(iv) Other Reactions

Semegen and Wakelin (12) in a study of the cross-linking of polyethyl acrylate suggest an acetoacetic ester mechanism for the reaction. The conditions they used, high temperatures (300° C.) and the presence of strong bases, are not comparable with those used in this work and it must be noted that alcohol is produced by thermal cracking of polyacrylates themselves. (The depolymerization of thermally unstable methacrylates cannot be regarded as supporting their theory.) It should be pointed out, however, that

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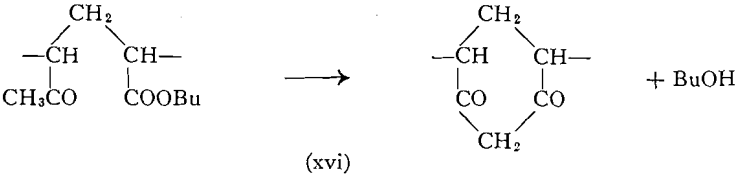
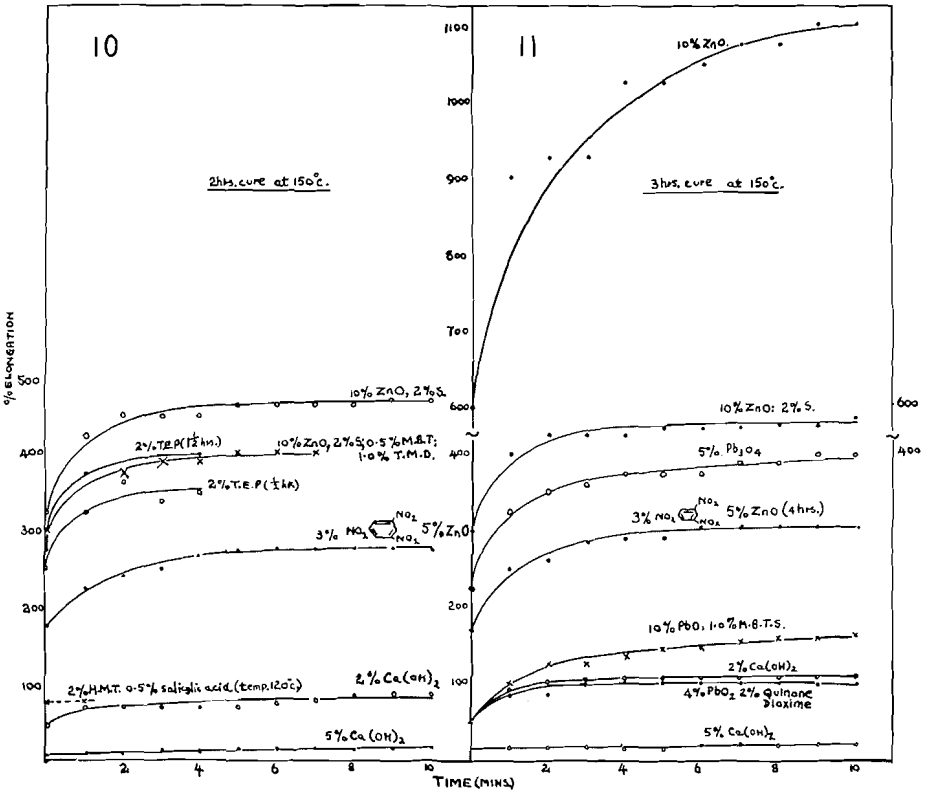
as yet no alternative mechanism has been suggested for the cross-linking of polyacrylates by bases such as potassium hydroxide.

In view of this it is therefore desirable to consider the possibility of a reaction of the following type (xvi) occurring.



(xvi)

The model compound *n*-butyl 5-ketohexoate was synthesized. Heating it alone or with sulphur at 150° C. produced no significant change, from which it may be inferred that there is no enhanced reactivity in the copolymer between adjacent MVK–acrylate units. On the other hand, heating with lead oxide at this temperature gave a fairly rapid reaction with liberation of butanol and the formation of a sticky solid soluble in chloroform, which proved to be mainly the lead salt of 5-ketohexoic acid. No evidence was found for dimethyl dihydroresorcinol, and it must be concluded that this reaction does not take place at vulcanization temperatures. A point of interest was the speed of hydrolysis by lead oxide.



FIGS. 10 AND 11.

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Comparison with Other Cross-linking Systems

It was thought desirable to compare the effect of the sulphur + zinc oxide system with some of the other compounds which may be used to cross-link polyacrylates.

Compounded samples were heated for various times and subsequently extended under constant initial load per unit area, and the elongation (instantaneous and after various periods of time) measured. A full program, varying the conditions of cure and using a combination of several curing agents, would be necessary to obtain the optimum properties in the vulcanizates. However, the results obtained show the general order of activity of the reagents used (Figs. 10 and 11).

It was found that calcium hydroxide and lead dioxide + quinone dioxime gave the fastest cures, but that the sulphur + zinc oxide combination gave the best formed vulcanizates. The latter were comparable to those obtained using polyamines, but had a lesser tendency to reversion on heating. Paraformaldehyde and HMT gave very rapid cures, the polymers not then altering on further heating. Paraformaldehyde gave highly blown products and is thus of little value, but HMT would appear to be suitable as a fugitive curing agent. In the case of most of the other systems, particularly those containing lead oxides, the hardening on heating is progressive, as shown by the data in Table V.

TABLE V

System	Elongation, %	
	1 hr. (at 150° C.)	7 hr. (at 150° C.)
Accelerated S, ZnO	450	310
Pb_3O_4	400	200
PbO_2 + QD	175	45
PbO	200	35
$Ca(OH)_2$	80	—
HMT	85*	65
TEP	350†	400†

* $\frac{1}{2}$ *hr.*
†$1\frac{1}{2}$ *hr.*

CONCLUSIONS

The effect of methyl vinyl ketone in promoting the cross-linking of its copolymers with *n*-butyl acrylate by alkaline reagents or by sulphur + zinc oxide appears to depend initially on the cyclization of adjacent ketone monomer units. These furnish water which, particularly in the presence of metallic oxides, enables hydrolysis to occur and thus form a three-dimensional network with metal salt bridges. In the presence of sulphur, attack occurs on the unsaturated ketone formed by the cyclization reaction with the formation of disulphide cross-linkages and zinc mercaptide cross-links. Zinc oxide also takes up the hydrogen sulphide formed in the reaction but has in itself only a weak cross-linking action. There is no evidence to support the view that direct attack occurs on the skeletal hydrogen atom adjacent to the carbonyl group.

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No reaction occurs between sulphur and the ester part of the molecule, and nothing to suggest acetoacetic ester condensation reaction has been observed. Emulsion copolymers have been found to be much more readily cyclized than copolymers prepared in solution, probably because of the presence of traces of alkali. This influences both the ease with which they are cross-linked and the aging resistance of the copolymers.

APPENDIX

Analysis of MVK–Acrylate Copolymers

As stated in the text the satisfactory analysis of these copolymers proved to be a task of some difficulty. Several methods were tried with the following results:

1. *Hydrolysis.*—A solution of the copolymer in dioxan, aqueous alcohol, or dioxan–benzene gave homogeneous solutions with alcoholic potash in the cold. On heating, the polymer was wholly precipitated from solution (even when containing as little as 5–10% of combined ketone). Before heating, hydrolysis was clearly incomplete, whereas on boiling, the skin of polymer formed caused the results to be poorly reproducible. It was established that no alkali was associated with the insolubilized polymer, and, in fact, many of the results (consistent between themselves) gave high values for the acrylate content. It is possible that under the influence of the alkali a variable amount of oxidation to carboxylic acid occurred, and in some cases lower acrylate contents were found using a nitrogen atmosphere. Attempts to carry out the hydrolysis in sealed containers or pressure vessels at 100–120° C. gave less reproducible results and dark-brown precipitates of polymer were formed. The results obtained were broadly in agreement with those obtained by other methods, but the lack of reproducibility obtained at present between repeat determinations on the same polymer makes the method unreliable.

2. *Infrared spectroscopy.*—Films cast from chloroform on to rock salts show overlapping of the carbonyl frequencies (1720 and 1740 $cm.^{-1}$) but here and with the 1440–1460 $cm.^{-1}$, 1400 $cm.^{-1}$, and 1070–1120 $cm.^{-1}$ bands, it was possible to carry out a determination of the ester contents with an accuracy of $\pm 5\%$.

3. *Refractive index measurements.*—In this method the basic assumption is that there is a linear relationship between refractive index and copolymer composition. It is possible that the relationship is curved but this cannot be verified until an absolute method has been obtained for determining the polymer composition. In fact, *a priori*, if Newton's law for the refractive index of mixtures holds, a linear relationship between molar composition and refractive index would be expected. A linear relationship between refractive index and weight composition has, of course, been found for butadiene–styrene copolymers (9), and, as it is reasonable to assume that there would be no interaction between adjacent ketone and ester groups, the deviation from linearity for the MVK copolymers should be small. Further evidence that refractive index measurements are satisfactory for copolymer analysis comes from the

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fact that copolymers of ethyl vinyl ketone and methyl *iso*propenyl ketone, which can be analyzed accurately by oximation, give linear composition – refractive index changes (1). Refractive indices were measured on a series of low conversion (*ca.* 10%) copolymers. The polymerizations were carried out at 70° C. using a 50% solution of monomers in benzene and 0.25% benzoyl peroxide as initiator. Films were cast on glass plates and, after being thoroughly dried (at 10^{-2} mm. at 60–70° C.), were pressed directly on the upper prism of an Abbé refractometer. Those polymers containing 60% or more of MVK were warmed in order to obtain optical contact with the prism. Measurements were carried out at 25° C. using white light. Typical results obtained are shown in the following table. The accuracy of measurement was about 2×10^{-4} unit for the higher acrylate content polymer, and 5×10^{-4} unit for those of high ketone content. The values for the two pure polymers were obtained from a number of measurements carried out on polymers prepared in bulk, in emulsion, and in solution. In the examination of several

TABLE

Sample	Mole fr. MVK (monomer)	η_{25}	$\Delta n \times 10^4$	Mole fr. MVK (polymer)
1	1.000	1.5025	370	1.00
2	0.875	1.4981	326	0.93
3	0.725	1.4915	260	0.81
4	0.630	1.4875	220	0.73
5	0.535	1.4832	176	0.62
6	0.310	1.4750	95	0.39
7	0.250	1.4738	83	0.35
8	0.090	1.4679	24	0.11 (5)
9	0	1.4655	0	0.00

samples of polymethyl vinyl ketone it was observed that one, obtained from B.A.S.F. Germany, gave slightly yellow colored polymers possessing a higher refractive index than normal (η_{25} 1.5137). Attempts to prevent this discoloration by fractionation of the monomer were not successful, but it was observed that on keeping, a quantity of cross-linked "popcorn"-like polymer formed throughout the commercial product. MVK recovered from the partly polymerized mass then gave polymers of normal refractive index. The ultraviolet spectra of the colored polymers and copolymers showed them to possess considerably greater absorption over the range 250–400 mμ and no appreciable maximum (pure polymethyl vinyl ketone possesses a maximum at 280 mμ and negligible absorption above 330 mμ). The cause of the differences has not yet been elucidated but is most probably due to copolymerization of impurities possessing two or more double bonds; the impurities would be concentrated in the low conversion copolymers examined.

Oximation

Quantitative oximation by a modification of the method of Trozzolo and Lieber (14) has been found to give satisfactory results with polymethyl *iso*-

propenyl ketone and polyethyl vinyl ketone, while polyethyl *iso*propenyl ketone does not react at all. MVK copolymers react readily but the tendency for the solutions to darken renders the end point difficult to observe and electrometric titration was employed. The main disadvantage of the method is the danger that a small amount of hydrolysis or oxamidation of the ester groups may occur. (It has been established, however, that no such reactions occur with polybutyl acrylate (1).)

Results obtained by the different methods on three copolymers are listed below. It can be seen that notwithstanding the scatter they are of the same order.

		% Butyl acrylate		
Polymer	Hydrolysis	Infrared	Refractive index	Oxime
A	24	20	19	25
B	28	25	22	—
C	47	40	43	43

Reaction of Copolymers with Sulphur

A series of low conversion solution polymers and high conversion emulsion polymers were made with varying proportions of MVK. The polymers were carefully dried under vacuum and sulphur (4%) incorporated by milling or in solution. Samples (0.2–2.0 gm. depending on ketone content) were placed in a thermostat at 150° C. and a gentle stream of nitrogen passed through. The gases were passed through ammoniacal cadmium acetate for three hours. At the end of this period excess iodine was added and the sulphide determined volumetrically.

Similar measurements on the simple ketones were made normally using a molar ratio of ketone to sulphur of 10:1. The greater amounts of hydrogen sulphide precluded the use of cadmium acetate as absorbent because of the formation of dense precipitates of sulphide, not readily soluble in iodine. It was found better to absorb the hydrogen sulphide in alkali and to estimate the sulphur gravimetrically after oxidation to sulphate. (Iodometric estimation of sulphide was not possible, since traces of ketone carried over by the gas stream reacted with iodine in alkaline solution.) In a typical experiment using 0.155 gm. of sulphur in 5 ml. of cyclohexanone at 150° C. hydrogen sulphide was liberated steadily; in seven hours 25% of the sulphur was eliminated as hydrogen sulphide. At 130° C. and 100° C. the corresponding amounts were 3.6% and 0.3% respectively.

The authors thank Mr. W. H. T. Davison and Mr. C. E. Kendall for spectroscopic examination of the copolymers and Miss R. K. Smith who carried out much of the analytical work. This paper is published by permission of the Dunlop Rubber Company Limited.

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NOTES

THE OCCURRENCE OF 4-*O*-METHYL-D-GLUCURONIC ACID IN LEMON GUM

By G. G. S. Dutton

The natural occurrence of 4-*O*-methyl-D-glucuronic acid was first reported in 1948 when it was found to be a component of mesquite gum (5, 6) and it is now known to occur elsewhere (3). Lemon gum has been shown (1) to contain L-arabinose, D-galactose, and a methoxyuronic acid. While this work was in progress there have appeared two papers concerned with the isolation of aldobiouronic acids from the gum. The first (4) reported the isolation of an aldobiouronic acid whose structure was thought to be 4-*O*-(D-glucuronosyl)-D-galactopyranose (I) on the basis of methylation studies. However, since the aldobiouronic acid contained an appreciable methoxyl content it is likely that the acid isolated was 4-*O*-(4[?]-*O*-methyl-D-glucuronosyl)-D-galactopyranose (II) which would give the same fragments as I on methylation and cleavage.

The second paper (2) reported the isolation from lemon gum of 4-*O*-(4-*O*-methyl-α-D-glucuronosyl)-L-arabinose. The nature of the uronic acid moiety was inferred from paper chromatographic analysis. The present work provides definite proof of the existence of 4-*O*-methyl-D-glucuronic acid in lemon gum.

Prolonged hydrolysis of lemon gum with hot sulphuric acid (0.2 *N*) removed arabinose units and afforded a degraded gum. Methanolysis (8% HCl) of the degraded lemon gum yielded a mixture of methyl glycosides from which methyl (methyl 4-*O*-methyl-D-glucopyranosid)uronate was isolated (5, 6). When this ester was treated with methanolic ammonia there was obtained a mixture of the α- and β-forms of methyl 4-*O*-methyl-D-glucopyranuronamide from which the α-form was readily obtained in a pure state by fractional crystallization. The amide of the α-anomer was characterized by comparison with an authentic specimen (5) and its identity further confirmed by conversion into 4-*O*-methyl-D-glucose from which the characteristic crystalline osazone was derived (5).

A preliminary examination of methylated lemon gum has shown the polysaccharide to have a highly branched structure in which the main chain is composed of D-galactose units. These results will be reported more fully at a later date.

EXPERIMENTAL

Lemon Gum

The gum was received from the late Dr. E. Anderson as small dark brown lumps and was used without purification except for the removal of bark by filtration of an aqueous solution. A sample of the purified gum after electrodialysis had $[\alpha]_D^{27}$ +21° and equiv. wt., 785.

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Methyl (Methyl 4-O-Methyl-D-glucopyranosid)uronate

Following the procedure of White (6) lemon gum (100 gm.) was hydrolyzed with sulphuric acid (0.2 *N*) and the degraded polysaccharide isolated by precipitation with ethanol after dialysis to remove arabinose and acid. The precipitated polysaccharide was refluxed with methanolic hydrogen chloride (8%), neutralized (Ag_2CO_3), filtered, and the filtrate evaporated to a thick sirup. Extraction of the sirup with acetone and ether (6) and evaporation of the solvents yielded a viscous sirup which was distilled under high vacuum. There was thus obtained methyl (methyl 4-*O*-methyl-D-glucopyranosid)-uronate (2.4 gm.) as a viscous, slightly yellow oil, b.p. 165–185°C. (0.1 mm.). Anal. Calc. for $C_9H_{16}O_7$: MeO, 39.4%. Found: MeO, 37.2%.

Methyl 4-O-Methyl-α-D-glucopyranuronamide

Methyl (methyl 4-*O*-methyl-D-glucopyranosid)uronate (2.3 gm.) was dissolved in methanol (5 ml.), and methanol saturated with ammonia at 0°C. (25 ml.) added. After the solution was kept at 5°C. for 36 hr. evaporation of the solvent and excess ammonia yielded a white solid.

The mixture of amides was recrystallized from methanol and yielded methyl 4-*O*-methyl-α-D-glucopyranuronamide. The crystals were washed with a little cold ethanol which preferentially removed the more soluble β-anomer. The amide had m.p. and mixed m.p. 236–237°C. and $[\alpha]_D^{23}$ +147° (*c*, 0.8 in water) (5). Anal. Calc. for $C_8H_{15}O_6N$: C, 43.5; H, 6.9; N, 6.3%; equiv. wt., 224. Found: C, 43.4; H, 6.9; N, 6.9%; equiv. wt., 228.

Methyl (Methyl 4-O-Methyl-α-D-glucopyranosid)uronate

Following the procedure of Smith (5) the α-form of the amide (1.33 gm.) was hydrolyzed to the acid and esterified with diazomethane. Distillation yielded the ester as a viscous oil (1.0 gm.), b.p. 145–160°C. (0.05 mm.). Anal. Calc. for $C_9H_{16}O_7$: MeO, 39.4%. Found: MeO, 39.2%.

4-O-Methyl-D-glucose

Methyl (methyl 4-*O*-methyl-α-D-glucopyranosid)uronate (220 mgm.) was dissolved in dry tetrahydrofuran (10 ml.) and slowly added with stirring to a solution of lithium aluminum hydride (500 mgm.) in dry tetrahydrofuran (25 ml.). After 15 min. at room temperature the excess hydride was destroyed by the addition of ethyl acetate and the inorganic salts precipitated by the addition of water. The mixture was filtered and the residue washed with ether. The combined ethereal solutions were evaporated to yield methyl 4-*O*-methyl-α-D-glucopyranoside as a colorless non-reducing sirup (110 mgm.) having $[\alpha]_D^{23}$ +121° (*c*, 2.0 in water). Hydrolysis of the glycoside with sulphuric acid (5 ml., 1 *N*) on a steam bath for six hours (constant rotation) and removal of the acid by passage through a column of Duolite A4 resin gave on evaporation 4-*O*-methyl-D-glucose (64 mgm.) as a colorless, reducing sirup having $[\alpha]_D^{23}$ +82° (*c*, 1.3 in methanol).

The 4-*O*-methyl-D-glucose (64 mgm.) was heated in water (2.5 ml.) containing acetic acid (0.25 ml.) at 70–80° for two hours with phenylhydrazine (0.2 ml.) and a few crystals of sodium hydrogen sulphite. On cooling, the reaction

mixture was poured into water and the precipitate isolated by centrifugation. Recrystallization from 25% aqueous acetone yielded 4-*O*-methyl-D-glucosazone as yellow needles, m.p. and mixed m.p. 158–159°C. (5).

ACKNOWLEDGMENT

The author is grateful to Dr. F. Smith for the gift of several samples and for his interest and advice while part of this work was carried out in the Department of Agricultural Biochemistry, University of Minnesota, St. Paul.

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THE MASS ASSIGNMENT OF THE CHAIN 2 MIN. Sb → 77.7 HR. Te → 2.25 HR. I

BY W. H. FLEMING AND H. G. THODE

The 77-hr. tellurium activity and its daughter 2.4-hr. iodine were first observed in fission by Abelson (1). He also showed that the 77-hr. activity grew in from a precursor of about five minutes' half-life, which might be antimony or some earlier member of the decay chain, and that the daughter of the iodine activity was either stable or had a half-life greater than several months. Katcoff *et al.* (3) showed that the 77-hr. tellurium had a mass of 132 or less from fission fragment range studies. Since definite assignments had been made for all β-active tellurium isotopes lighter than 132, the 77-hr. activity and its iodine daughter were assigned to the 132 mass chain. More recently Pappas and Coryell (4, 5) have given a value of 77.7 hr. for the half-life of Te^{132} and assigned a 2.0-min. antimony activity to Sb^{132} on the basis of energetic considerations. Emery and Veall (2) have carried out a careful determination of the half-life of I^{132} and report $2.250 \pm .003$ hr.

During the course of a determination of the fission yields of Xe^{133} at this laboratory, fission product xenon was extracted from neutron irradiated uranium and plutonium before all of the 77.7-hr. tellurium activity had decayed. By a comparison of the relative abundances of Xe^{132} and Xe^{134} in these samples with that observed when the irradiated material is allowed to stand for a time long compared to 77.7 hr., the effective half-life of the precursors of Xe^{132} can be determined assuming that there are no long-lived members in the 134 mass chain.

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If there is only one member in the 132 mass chain with a half-life comparable to the time of irradiation and cooling, the number of atoms of Xe^{132} present at the time of extraction is given by

$$[1] \qquad (Xe^{132})_{t_1} = R\left[T - \frac{(1-e^{-\lambda T})e^{-\lambda t_1}}{\lambda}\right]$$

where R is the production rate of the 132 mass chain

T is the time of irradiation

t_1 is the cooling time

λ is the disintegration constant of the long-lived chain member.

If the sample is allowed to cool for a time sufficiently long for all the precursors to decay, then

$$[2] \qquad (Xe^{132})_{\infty} = RT.$$

Thus from the mass spectrometer ratios of Xe^{132} to Xe^{134} measured for samples extracted after short and long cooling and from equations [1] and [2] the disintegration constant λ can be calculated from:

$$\frac{(Xe^{132}/Xe^{134})_{t_1}}{(Xe^{132}/Xe^{134})_{\infty}} = \frac{(Xe^{132})_{t_1}}{(Xe^{132})_{\infty}} = 1 - \frac{(1-e^{-\lambda T})e^{-\lambda t_1}}{\lambda T}.$$

The details of the five separate irradiations used to determine λ are given in Table I.

TABLE I

Sample	Irradiation time T (hr.)	Cooling time t_1 (hr.)	$\frac{(Xe^{132})_{t_1}}{(Xe^{132})_{\infty}}$	Disintegration constant λ (hr.$^{-1}$)
1	59.0	124.0	0.753	0.00918
2	60.0	147.8	0.814	0.00955
3	48.0	92.8	0.669	0.00954
4	48.0	166.0	0.804	0.00861
5	48.0	139.9	0.780	0.00927
Average	—	—	—	0.00923±.00034

Greater accuracy could have been obtained if the extraction of xenon had been carried out when less of the 77.7-hr. activity had decayed.

The half-life corresponding to the average value of λ is 75±3 hr. This mass spectrometric detection of a precursor of Xe^{132} having a half-life of about 75 hr. is direct confirmation of the assignment of the 77.7-hr. tellurium activity (and its daughter 2.25-hr. iodine) to the 132 mass chain.

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THE NUMBER OF SUBUNITS IN THE MOLECULE OF HORSE HEMOGLOBIN[1]

BY M. E. REICHMANN[2] AND J. ROSS COLVIN

ABSTRACT

The molecular weights of horse hemoglobin, horse globin, and performic acid oxidized horse globin were determined by osmotic pressure, by an approach to equilibrium sedimentation, and by light scattering (except hemoglobin) at pH 1.5 to 2.5 in 0.05 *M* NaCl. Sedimentation coefficients were determined for these materials over the same pH range and electrophoretic analyses were made from pH 1.5 to 4.0. The results show that in dilute salt solutions below pH 2.5 horse hemoglobin dissociates to four subunits all approximately equal in mass but at least two of which differ electrokinetically and therefore in composition. The subunits are probably held together in the native hemoglobin molecule only by non-covalent bonds.

INTRODUCTION

The effect of changes in pH of the medium upon the size, shape, and dissociation of a number of proteins has contributed to knowledge of their structure (11). In particular, the properties of mammalian hemoglobins in dilute acid solutions (13), in surface films (14), in solutions of urea (34), and in concentrated salt solutions (15) have indicated that the molecules may split into halves or smaller subunits. These observations, coupled with the presence of four hemes per molecule, have led to the plausible conclusion that there are four subunits in each hemoglobin (17), but definitive evidence has been lacking. In addition, Porter and Sanger's (27) observation of six N-terminal valine residues in horse hemoglobin suggests that, in some species, the subunits may be further dissociated to individual polypeptides or that branching of one or two chains occurs. To test previous conclusions, and to distinguish between the above possibilities, the molecular weights of horse hemoglobin, horse globin, and performic acid oxidized horse globin have therefore been determined by light scattering, osmotic pressure, and Archibald's approach to equilibrium sedimentation (5), at higher hydrogen ion concentrations than reported hitherto. The results were supplemented by velocity sedimentation and electrophoretic analyses.

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Contribution from the Division of Applied Biology, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 3877.
[2]*National Research Council Postdoctorate Fellow, 1953–54, 1954–55; present address, Science Service, Department of Agriculture, Ottawa.*

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MATERIALS AND METHODS

Crystalline horse hemoglobin was prepared by the method of Heidelberger (19). The filter cake of twice recrystallized oxyhemoglobin was stored frozen until used. All the filter cake dissolved in water at 0°C. except a small fraction of white flocculent material which was removed by centrifugation before preparation of the globin. Two determinations of the sedimentation coefficient of the sample, $S_{w,20}$, in 0.05 *M* phosphate, pH 6.8, at concentrations of 0.25% and 0.50%, gave 4.40×10^{-13} and 4.54×10^{-13} respectively. These values are in agreement with previous results (37). An electrophoretic analysis of a 0.2% solution of the hemoglobin in 0.05 *M* phosphate at pH 6.8, time 141 min., gave a single, slowly migrating peak for both ascending and descending boundaries. The molecular weight of the hemoglobin by osmotic pressure in 0.1 *M* NaCl, pH 7.0, was 65,000.

Globin was prepared by Anson and Mirsky's method (4) as modified from Jope, Jope, and O'Brien (22). Crystalline horse oxyhemoglobin was dissolved in ice water to give a 5% solution and the supernatant poured, with rapid stirring, into 10 times its volume of 0.7% HCl–acetone at −15°C. The precipitate was removed by filtration at −15°C. and most of the heme washed out at that temperature by HCl–acetone, followed by chilled acetone. The precipitate was redissolved in ice water, reprecipitated and washed again, as above, three times. After the final washing with acetone, the precipitate was dissolved in ice water, filtered through coarse filter paper, and freeze dried. The product, which was always a light tan in color, was initially soluble in water and 0.05 *M* NaCl but reprecipitated quickly if the pH was between 4.0 and 10.0. Outside this range, solutions of globin, 1% or lower in concentration, were stable indefinitely in 0.05 *M* NaCl. Increasing the salt concentration decreased solubility at all pH values. Native horse globin, in the sense that all the product was soluble indefinitely close to neutrality, was not obtained, in agreement with previous observations of the particular instability of horse globin (31).

A modification of Sanger's method (33) was used to oxidize any disulphide bridges in globin and thus promote separation of the polypeptide chains. Each gram of unoxidized globin was dissolved in 36 ml. of 90% formic acid to which 6 ml. of 30% H_2O_2 had been added one hour before. The mixture was allowed to stand at room temperature for 25 min. (one sample was over-oxidized by extending the time to 60 min.) and then poured into 10 times its volume of 0.7% HCl–acetone at −15°C. The precipitate was removed by rapid centrifugation at room temperature, immediately dissolved in water, and dialyzed against water for 48 hr. at 5°C., with frequent changes of the external solution. The resulting optically clear solution was then centrifuged and freeze dried. The solubility properties of the white product were similar to those of unoxidized globin except that the oxidized material was initially more readily soluble in water or dilute buffer solutions but also reprecipitated more quickly. Control experiments established that less than 2% of the initial nitrogen was lost during oxidation of the globin.

Only valine was detected as an N-terminal amino acid residue in both the

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unoxidized and oxidized globin by the DNFB technique (26). Since Porter and Sanger had previously found only valine as an N-terminal residue in horse hemoglobin (27) this observation is evidence that no appreciable degradation of the polypeptide chains occurred during the oxidation procedure. Other investigations have also shown that the peptide bond is resistant to attack by performic acid (3).

Both unoxidized and oxidized samples of globin were prepared for examination by dissolving the sample in water or the appropriate buffer, followed by dialysis against 10 times the volume of the buffer changed frequently.

All buffers were prepared from reagent grade materials by Clark's procedure (9) and checked frequently against commercial standards with a Beckman Model G pH meter. Where necessary, the pH of solutions of sodium chloride was adjusted by the addition of small amounts of HCl.

Crystallized bovine plasma albumin and crystallized bovine pancreas ribonuclease were used as purchased from Armour and Company, Chicago.

The techniques of molecular weight determination by light scattering were as previously described by one of us (28). All measurements were made at a wavelength of 4360Å. A monochromatic filter was also inserted in the phototube mouthpiece to eliminate fluorescent light. The refractive index increment, dn/dc, of unoxidized globin was measured in the Brice and Speiser differential refractometer (7) and found to be 0.200 ± 0.003 in 0.2 M NaCl, pH 2.5. With this value of dn/dc, K (28) had the value of 6.46×10^{-7}. The same figure was used for oxidized globin.

Osmotic pressures were determined by the equilibrium method. The osmometers as well as the technique used were as previously described (29). Determinations of the molecular weight of bovine plasma albumin in 0.1 M NaCl, pH 6.5, gave 68,000 in agreement with previously reported results (16). Prior adjustment of the osmotic pressure to close to the estimated final equilibrium value, which was then maintained for 12 hr. or more, showed the membranes to be impermeable to any component of the globin or hemoglobin preparations. The same technique showed that the membranes were readily permeable to ribonuclease, molecular weight 13,000.

Sedimentation coefficients were determined in a Spinco Model E ultracentrifuge at 250,000 g using a plastic cell to contain the more acid solutions. Boundary displacements were read directly from the photographic plates by a microcomparator accurate to ± 0.001 mm., but this overestimates the precision since rapid diffusion of the peak made the exact position of the mode uncertain. In calculating $S_{w,20}$, a 1° correction for adiabatic cooling of the rotor (6, 36) was applied as well as the usual adjustments for temperature and viscosity of the buffer (2). Three determinations of the $S_{w,20}$ of bovine plasma albumin in 0.05 M phosphate buffer, 0.2 M NaCl, pH 6.6, at concentrations 0.33%, 0.50%, and 1.0% gave the values 4.10, 4.08, and 3.91×10^{-13} respectively in agreement with previous results (24).

Molecular weights were determined by an approach to equilibrium sedimentation using Archibald's method (5) as recently applied by Brown, Kritchevsky, and Davies (8). All measurements were made at a rotor speed of 12,590 r.p.m.

The molecular weight of globin was calculated from the extrapolated values of $(1/rc)(dc/dr) = \delta = M\omega^2(1-V\rho)/RT$ (M = weight average molecular weight, ω = angular velocity, V = partial specific volume of protein, ρ = density of solution, R = gas constant, and T is the temperature) using the partial specific volume, 0.749, as reported for hemoglobin (37).

Concentrations of protein were estimated by micro-Kjeldahl, using Tristram's value for the nitrogen content of hemoglobin (35). The error in the nitrogen determination was less than 1% of the total nitrogen present.

Electrophoretic analysis was conducted in a constant current Tiselius apparatus as modified by Longsworth (23). Mobilities of the peaks were calculated by standard methods (1) from the migration distances of the descending boundary read directly from the plates. All peaks could usually be recognized on both ascending and descending boundaries, although, as usual, resolution was better on the ascending side.

RESULTS

Molecular Weight of Unoxidized and Oxidized Globin by Light Scattering

Preliminary investigation showed that above pH 2.5, aggregation of unoxidized and oxidized globin was considerable. Even at pH 2.5, in 0.2 M NaCl the negative second virial coefficient of the plot of Kc/R_{90} against concentration for unoxidized globin showed that interparticle attractive forces are greater than the Coulomb repulsion (Fig. 1). The apparent molecular weight under these conditions was 39,000. In 0.05 M NaCl at pH 2.65 for the same material the coefficient is slightly positive and the apparent molecular weight was 37,000 (Fig. 1). Fig. 2 shows corresponding data for unoxidized globin at pH 1.5 and 2.0 in 0.05 M sodium chloride. Taking the widest reasonable range of estimates of the intercepts, the molecular weight remains at about 21,000–23,000. Net interactions are not large as shown by the small second virial coefficient. Light scattering data for the oxidized globin in 0.05 M NaCl at pH 2.5 and 2.0 are shown in Fig. 3. At pH 2.5 the weight average molecular weight of the oxidized globin, 41,000, is approximately equal to that of the unoxidized material. However, contrary to the results for unoxidized globin, no further decrease in molecular weight was apparent at pH 2.0.

Molecular Weight of Hemoglobin, and of Unoxidized and Oxidized Globin by Osmotic Pressure

Osmotic pressure data for hemoglobin and oxidized globin at pH 1.8, and for unoxidized globin at pH 2.0, in 0.05 M NaCl are given in Fig. 4. The number average molecular weight of hemoglobin from the extrapolated value of P/cRT was $20{,}000 \pm 1000$, of oxidized globin about 21,000, and of unoxidized globin $16{,}000 \pm 1000$.

Velocity Sedimentation

Above pH 2.5 or in salt solutions above 0.05 M the sedimenting boundaries of solutions of unoxidized and oxidized globin became skew or separated into

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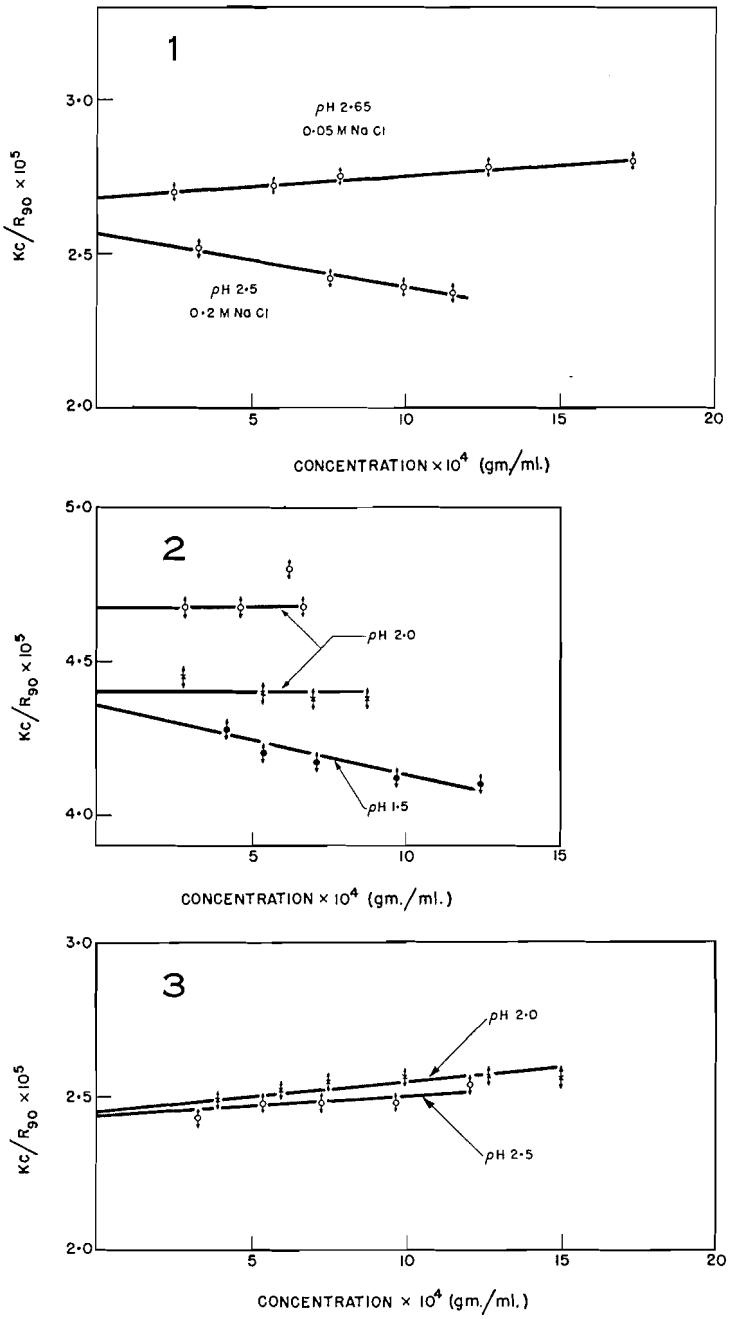

FIG. 1. Light scattering data for unoxidized globin, under two conditions of sodium chloride and hydrogen ion concentration.

FIG. 2. Light scattering data for unoxidized globin in 0.05 *M* sodium chloride at pH 1.5 and 2.0. The points shown for experiments at pH 2.0 give the maximum range observed.

FIG. 3. Light scattering data for oxidized globin in 0.05 *M* sodium chloride.

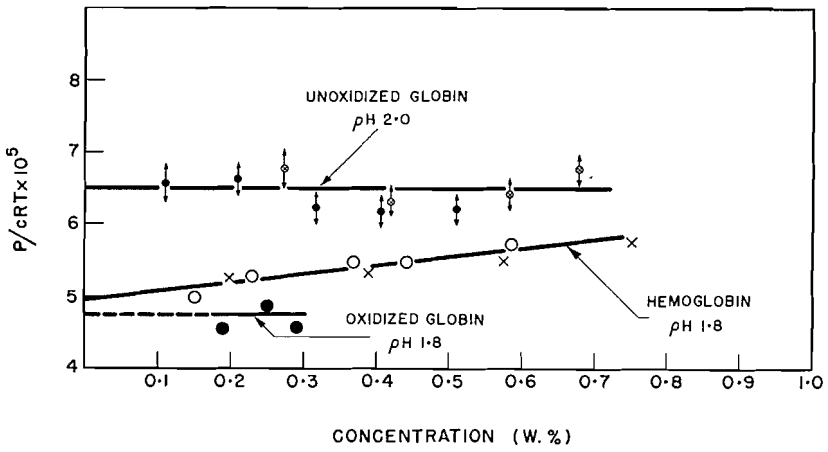

FIG. 4. Osmotic pressure data for hemoglobin, and for unoxidized and oxidized globin in 0.05 *M* sodium chloride.

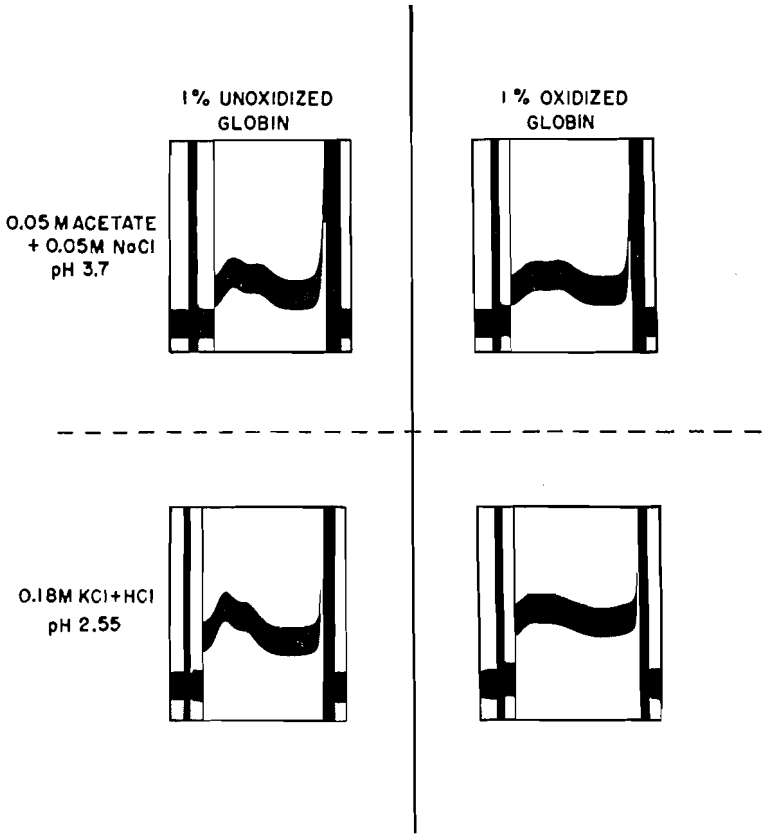

FIG. 5. Photographs of refractive index gradient distributions in velocity sedimentation of unoxidized and oxidized globin under two conditions.

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poorly resolved peaks (Fig. 5). These features disappeared progressively upon decreasing the pH or salt concentration, thereby eliminating the possibility that they were evidence for stable components. At or below about pH

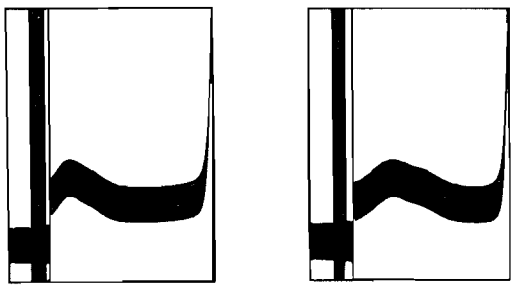

FIG. 6. Photographs of refractive index gradient distributions of unoxidized globin in 0.05 *M* sodium chloride.

2.5, the sedimenting peak for unoxidized globin was single, broad, and less asymmetric (Fig. 6) and the sedimentation coefficient was constant within experimental error (Table I). Its value is approximately one half that given by Gralén for the same material at pH 4.0 (13).

TABLE I

THE SEDIMENTATION COEFFICIENT OF UNOXIDIZED HORSE GLOBIN IN 0.05 *M* NaCl AS A FUNCTION OF pH

pH	Concentration, %	$S_{w,20}$
1.50	0.8	1.08×10^{-13}
1.65	1.0	1.20
2.05	1.0	1.09
2.10	1.0	1.18
2.50	1.0	1.29
		Mean 1.17×10^{-13}

TABLE II

THE SEDIMENTATION COEFFICIENT OF UNOXIDIZED HORSE GLOBIN IN 0.05 *M* NaCl, pH 2.5, AS A FUNCTION OF CONCENTRATION

Concentration, %	$S_{w,20}$
0.3	1.43×10^{-13}
0.5	1.30
0.7	1.38
1.0	1.29

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Table II gives the sedimentation coefficient of unoxidized globin in 0.05 *M* NaCl, pH 2.5, as a function of concentration. Clearly the coefficient is not a marked function of concentration under these conditions.

Tables III and IV give the results of a determination of the sedimentation coefficient of oxidized globin as a function of pH and concentration respectively. Table IV also gives the same data for a sample of overoxidized globin.

TABLE III

THE SEDIMENTATION COEFFICIENT OF OXIDIZED GLOBIN (1.0%), IN 0.05 *M* NaCl, AS A FUNCTION OF pH

pH	$S_{w,20}$
1.65	1.65×10^{-13}
2.05	1.44
1.65	1.68
2.9	1.62

TABLE IV

THE SEDIMENTATION COEFFICIENT OF OXIDIZED AND OVEROXIDIZED GLOBIN IN 0.05 *M* NaCl, pH 2.5, AS A FUNCTION OF CONCENTRATION

Conc., %	$S_{w,20}$
Oxidized globin	
0.3	1.83×10^{-13}
0.5	1.61
0.7	1.73
	Mean 1.72×10^{-13}
Overoxidized globin	
0.3	2.87×10^{-13}
0.5	2.82
0.7	2.72
	Mean 2.80×10^{-13}

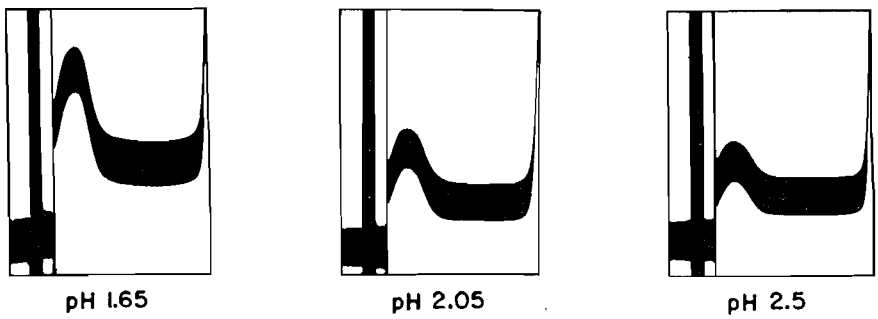

FIG. 7. Photographs of refractive index gradient distribution of oxidized globin in 0.05 *M* sodium chloride.

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Typical patterns are shown in Fig. 7. The sedimentation coefficient of oxidized globin is not a strong function of either pH or concentration but the coefficient of the overoxidized sample is nearly double that of the less drastically treated one.

To assess the effect of removal of the heme groups on the sedimentation coefficient, the $S_{w,20}$ of hemoglobin was determined as a function of concentration at pH 2.5 in 0.05 *M* NaCl and in 0.2 *M* NaCl. Results are given in Table V.

TABLE V

THE SEDIMENTATION COEFFICIENT OF HORSE HEMOGLOBIN AT pH 2.5 IN 0.05 *M* NaCl AND 0.2 *M* NaCl AS A FUNCTION OF CONCENTRATION

0.05 *M*		0.20 *M*	
Conc., %	$S_{w,20}$	Conc., %	$S_{w,20}$
0.1	1.64×10^{-13}	0.1	3.26×10^{-13}
0.2	1.65	0.2	3.35
0.3	1.95	0.3	2.84

At pH 2.5 in 0.05 *M* NaCl the coefficient for hemoglobin is higher than for unoxidized globin but is comparable to that for oxidized globin (Table IV). Increasing the sodium chloride concentration to 0.2 *M* doubled the coefficient for hemoglobin.

This increase in sedimentation coefficient with increasing salt concentration may be attributed to either reassociation of subunits *or* a decrease in the electrostatic repulsion of subunits, without association. To distinguish between these possibilities, the sedimentation coefficient of ribonuclease was determined as a function of concentration in 0.05 *M* NaCl, pH 2.5. Ribonuclease was chosen because it has an isoelectric point close to that of hemoglobin (32), a molecular weight comparable with that of the suspected subunit of hemoglobin (10, 11), and is known to consist of one polypeptide chain (3). Results are given in Table VI. The mean value 1.85×10^{-13} at pH 2.5 is

TABLE VI

THE SEDIMENTATION COEFFICIENT OF RIBONUCLEASE IN 0.05 *M* NaCl, pH 2.5, AS A FUNCTION OF CONCENTRATION

Conc., %	$S_{w,20}$
0.3	1.89×10^{-13}
0.5	1.86
0.7	1.81
	Mean 1.85×10^{-13}

in excellent agreement with that for ribonuclease close to neutrality, 1.85×10^{-13} (11). These results suggest that the direct electrostatic effects upon the sedi-

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mentation coefficient of hemoglobin and globin may be neglected, even under these rather drastic conditions and that the increasing sedimentation coefficient reflects increasing aggregation.

Equilibrium Sedimentation

The results of applying Archibald's procedure (5), for estimating equilibrium ultracentrifuge molecular weights, to unoxidized globin in 0.05 *M* NaCl, pH 2.0, are summarized in Fig. 8. The estimated values of δ are equal at the base and at the meniscus of the cell and correspond to a molecular weight of 22,000. Hemoglobin under the same conditions was polydisperse with an apparent molecular weight of about 23,000 at the meniscus and 50,000 at the base.

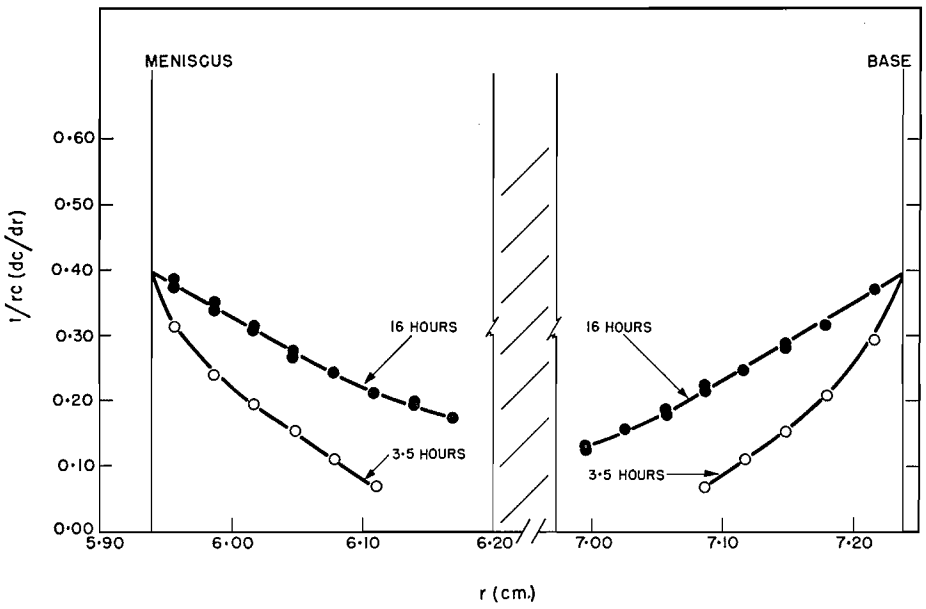

FIG. 8. Archibald's approach to equilibrium sedimentation for unoxidized globin in 0.05 *M* sodium chloride, pH 2.0.

Electrophoresis

Unoxidized and oxidized globin showed similar complex behavior when examined electrophoretically from pH 4.0 to pH 1.5 in dilute buffer or salt solutions. Resolution of the apparent components was better in the unoxidized material, however, presumably because of a decrease in the isoelectric point of the oxidized globin imposed by newly introduced negative groups. Increasing the salt concentration from 0.05 *M* to 0.2 *M* NaCl decreased resolution of some peaks in the pattern or eliminated them completely. At pH 4.0 in 0.05 acetate and 0.05 *M* NaCl, one large peak was observed, accompanied by a slower, smaller component (Fig. 9). In some experiments, this slower peak could not be resolved and only one peak was apparent, particularly at higher salt con-

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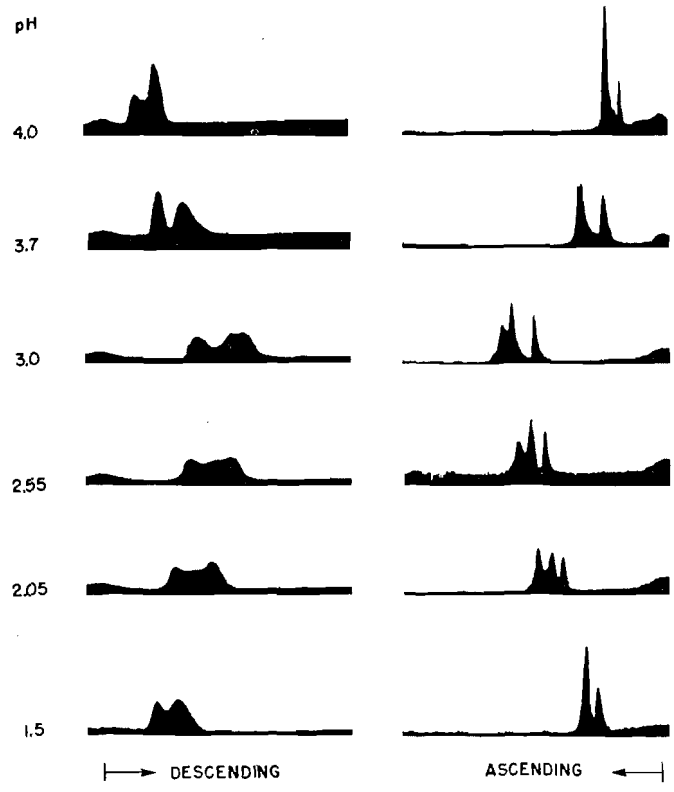

FIG. 9. Electrophoretic patterns of unoxidized globin in 0.05 *M* sodium chloride as a function of pH. At pH 3.7 and 4.0, the solutions contained 0.05 *M* acetate in addition to the sodium chloride.

centrations. As the pH decreased to 3.7 the apparent proportion of this slower component increased until the concentration of both components was approximately equal. These were presumed to be the two components previously observed in the hemoglobin of other species (18, 25, 30) at high hydrogen ion concentrations. A further decrease in pH was attended by separation of a third, faster component until at pH 2.5 the apparent concentrations of all three were approximately equal. Finally between pH 2.0 and 1.5, one component disappeared leaving only two well-defined peaks. Similar variation of components with pH was shown by the untreated horse hemoglobin. Approximate estimates of the mobilities of the three components of unoxidized globin in the descending boundary are given in Fig. 10 as a function of pH. Within experimental error the mobility of the intermediate peak remains constant from pH 1.5 to 4.0 while that of the slowest goes through a maximum at about pH 3.0. The mobility of the fastest peak apparently decreases from pH 3.0 where it is first evident to pH 2.0 below which it either disappears or incorporates all of the material of intermediate mobility.

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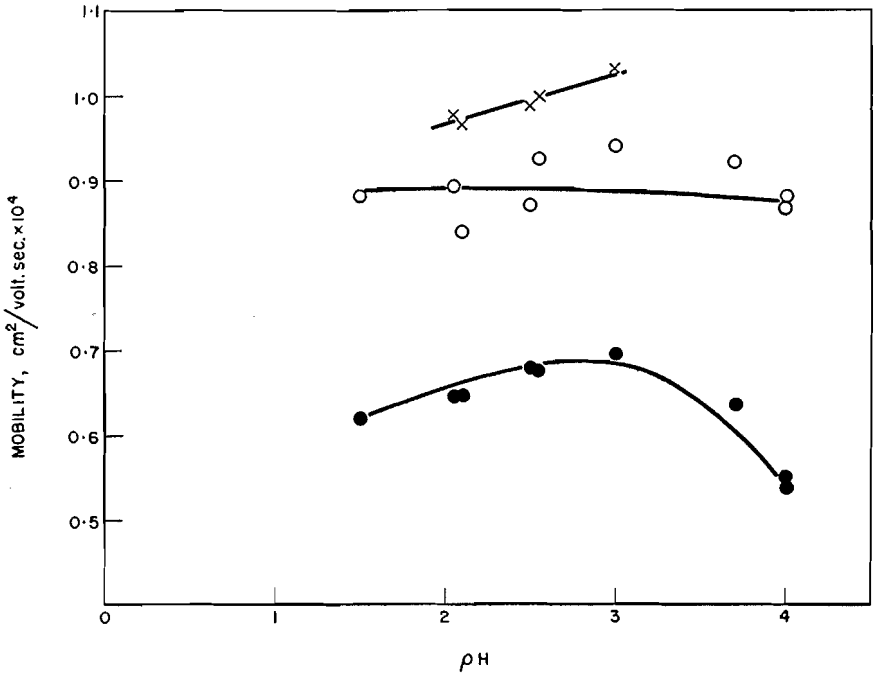

FIG. 10. Estimates of the mobilities of the three apparent components of unoxidized globin as a function of pH.

DISCUSSION

The foregoing data from light scattering, osmotic pressure, and sedimentation velocity show that a net effect of oxidation of globin by performic acid is to *increase* the molecular weight of the material, at a given pH level, rather than decrease it, as would be expected if covalent bonds were being broken. The increase therefore implies that disulphide bonds do not link polypeptide chains in horse hemoglobin, in agreement with conclusions from sulphydryl determinations (21). The higher molecular weight may be attributed to reassociation of the subunits of hemoglobin, following reduction of their isoelectric points by the additional sulphonic acid groups. Since horse hemoglobin contains a negligible percentage of phosphorus (18, 38) it is therefore probable that the polypeptide chains are held together in the molecule only by secondary bonds or by mechanical entanglement.

The difference between the number average molecular weight and the weight average value for unoxidized globin in 0.05 *M* NaCl at pH 1.8–2.0, together with the ill-defined peaks and rapid spreading of the sedimenting boundary in the ultracentrifuge at higher pH levels, shows that the solutions are polydisperse. This heterogeneity must reflect an association of subunits of approximately equal size rather than a collection of independent particles of different molecular weights because (*a*) sedimentation velocity boundaries increase in symmetry as the pH decreases, (*b*) only the assumption of dissociation products of equal size is compatible simultaneously with the observed

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molecular weights and the observation that the products do not pass a membrane which is readily permeable to ribonuclease. At pH 2.0 in 0.05 *M* NaCl however, the equilibrium point is far toward the side of dissociation as shown by the lack of effect of concentration change on $S_{w,20}$. For this reason, the observed number average molecular weight at pH 2.0, 16,000–17,000, will be a good approximation to the molecular weight of the dissociation products and indicates that the total number of dissociable subunits in the hemoglobin molecule under these conditions is four. A smaller number cannot account for the observed osmotic pressures and a larger number is incompatible with the retention of all the dissociation products by the membrane. The conclusion of four subunits of equal size in hemoglobin is likewise consistent with the approximately fourfold reduction in sedimentation coefficient of hemoglobin at pH 7.0 to that of globin at pH 2.0. These results therefore directly confirm previous inferences.* No evidence for further dissociation was found, even at pH 1.5. Consequently, unless two polypeptide chains are so closely intertwined as to prevent separation under these drastic conditions, Porter and Sanger's observation of six N-terminal amino acid residues in horse hemoglobin suggests that branching occurs in at least two of the polypeptide chains which comprise the subunits.

The equilibrium in the association between these subunits is not established instantaneously, as shown by the presence of transient and poorly resolved peaks in velocity sedimentation. It is complete, however, in 3.5 hr. at pH 2.0 as shown by the equality of δ for unoxidized globin at the base and the meniscus of the cell in the approach to equilibrium ultracentrifugation. Field and O'Brien have recently shown that the dissociation to half molecules is rapid in acid solution for human hemoglobin (12), in which the extent of splitting is much less than for horse hemoglobin (37). Consequently, these observations suggest that the dissociation of the horse hemoglobin molecule in acid solution takes place in two distinct stages under the influence of Coulomb repulsion; first a rapid, reversible dissociation to half molecules followed by a slower, not completely reversible separation of the components of the half molecules. This latter is probably the process to which the term denaturation has been applied (12).

As shown by velocity sedimentation, equilibrium sedimentation, and osmotic pressure experiments, heme tends to stabilize the association of the subunits of globin, even at pH levels far below 3.9, at which point the porphyrin ring begins to split from the protein (20).

The electrophoretic analyses show that the two half molecules of horse hemoglobin differ electrokinetically and also provide additional qualitative evidence for further splitting of half molecules into distinct subunits. No exact definitive interpretation of the patterns can be given but they are consistent with the assumption that at pH 4.0–3.7, the hemoglobin splits predominantly into half molecules of different mobilities. As the pH decreases,

**Gutter and Peterson have also very recently found indirect evidence for four subunits in horse hemoglobin from studies on the effect of mercaptoethanol and urea on the sedimentation rate, as reported at the American Chemical Society Meeting, Sept. 13, 1955, Minneapolis, Minn.*

an increasing proportion of both these half molecules dissociate to subunits. Of these four subunits, at least two must differ electrokinetically. If a larger number differ, they may reassociate to form new complexes of intermediate mobility. Such complexes would be an adequate explanation for the discordant observations reported on similar preparations of hemoglobins from other species (25, 30). Finally, at very low pH's (i.e. below 2.0), Coulomb repulsion is so strong between subunits that complex formation is repressed and the apparent number of components decreases.

One over-all conclusion from these experiments must be stressed. The tendency to association between the different subunits of the hemoglobin molecule is surprisingly strong, in spite of the absence of any covalent bonds and in opposition to Coulomb repulsion. This must confer a stability to the general configuration of the hemoglobin molecule, which may play a role in its physiological function.

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SOME XANTHATE METHYL ESTERS OF GLUCOSE[1]

By Amiya K. Sanyal[2] and C. B. Purves

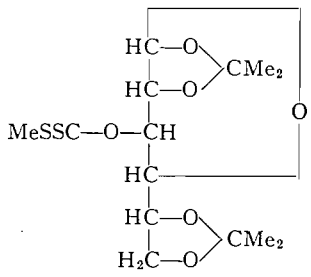
ABSTRACT

The following compounds were thought to be new: 1,2-mono-*O*-isopropylidene-D-glucofuranose-3-*S*-methyl xanthate, m.p. 102°, $[\alpha]_D^{24}$ −27.8°; methyl-4,6-*O*-benzylidene-α-D-glucopyranoside-2,3-di-*S*-methyl xanthate, m.p. 100°, $[\alpha]_D^{22}$ −18.1°; and 1,2;3,5-di-*O*-methylene-α-D-glucofuranose-6-*S*-methyl xanthate, m.p. 99°, $[\alpha]_D^{21}$ +27.3° in chloroform. Partial hydrolysis of the isopropylidene and methylene derivatives yielded some glucose-3-*S*-methyl xanthate and glucose-6-*S*-methyl xanthate as crude sirups. The 6-xanthate greatly excelled the 3-xanthate in stability toward acid. The chromatographic behavior of both was determined.

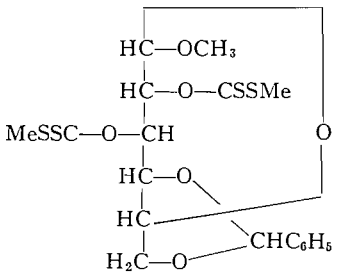
INTRODUCTION

Although xanthate salts are very readily decomposed by acid, a recent research (20) confirmed the claim that the *S*-methyl xanthate esters of simple alcohols are often remarkably stable in acidic conditions. The location of the substituents in cellulose sodium xanthates (viscose) might therefore be determined by conversion to the *S*-methyl esters, hydrolysis to the corresponding glucose derivatives, and identification of the latter. In order to explore this possibility, attempts have now been made to prepare some of the relevant glucose-*S*-methyl xanthates, to determine their stability toward acids and their behavior in chromatography.

In 1927 Freudenberg and Wolf (4) shook 3-sodio-1,2;4,5-di-*O*-isopropylidene glucofuranose first with carbon disulphide to form the 3-xanthate salt, and then with methyl iodide to obtain the crystalline 3-*S*-methyl ester (I). They



I



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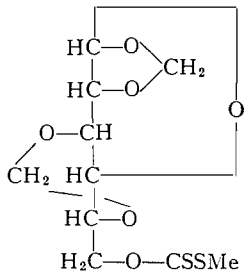

III

apparently did not succeed in selectively hydrolyzing the isopropylidene groups and therefore recovered neither glucose-3-*S*-methyl xanthate nor its monoisopropylidene derivative. A repetition of this work showed that the yield of I could be increased from 52% to nearly 90% of theory, based on the

[1]*Manuscript received December 9, 1955.*
Contribution from the Division of Industrial and Cellulose Chemistry, McGill University, and from the Wood Chemistry Division, Pulp and Paper Research Institute of Canada, Montreal, Que. Abstracted from a Ph.D. thesis submitted to the University by A.K.S. in August, 1953.
[2]*Present address: 12/1/4 Monoharpukar Road, Calcutta-26, India.*

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diisopropylidene glucose that reacted. The substance (I) was then submitted to acetolysis in an attempt to replace the isopropylidene by acetyl groups, as Hann, Hudson, and their numerous collaborators succeeded in doing with similar cyclic acetals (6, 13, 22). Although analyses suggested that some of the isopropylidene had indeed been replaced by acetyl groups, the impure product failed to crystallize, and eventually the method was abandoned. The diisopropylidene methyl xanthate was then hydrolyzed with concentrated nitric acid in ethyl acetate as described by Coles, Goodhue, and Hixon (2) for the removal of the 5,6-isopropylidene group from 1,2;5,6-di-*O*-isopropylidene glucofuranose, but some xanthate groups were lost and the product was an impure sirup. The realization that this xanthate ester was not nearly so resistant toward acidic reagents as those studied by Vincent (20) led to an attempt to prepare a more stable derivative by oxidizing I with 30% aqueous hydrogen peroxide in glacial acetic acid. Unlike Vincent's experience with octadecyl-*S*-methyl xanthate, this oxidation failed to yield a stable crystalline derivative retaining all of the original sulphur, but produced extensive decomposition. Details of these and other negative experiments have been omitted from this account.

Freudenberg, Dürr, and Hochstetter (3) found that boiling methanolic hydrogen chloride removed the isopropylidene group in the 5,6-position of diisopropylidene glucose 40 times more rapidly than the one in the 1,2-position. By restricting the action of a 0.15% hydrogen chloride solution to eight minutes, it was found possible to prepare a pure, crystalline mono-*O*-isopropylidene glucose-3-*S*-methyl xanthate from the diisopropylidene derivative in about 35% yield, 30% of the starting material being recovered unchanged. When chromatographed on paper, using *n*-butanol saturated with water as the solvent and ammoniacal silver nitrate as the spray, the mono- and diisopropylidene methyl xanthates had R_f values of 0.92 and 0.97, respectively. The former compound produced a yellow spot with the spray immediately, but the latter developed a dark gray spot only after the paper had been heated at 100° for a few minutes. The two compounds could therefore be distinguished readily.

In order to study the hydrolysis of the monoisopropylidene methyl xanthate, a 2% solution in 0.05 *N* aqueous hydrochloric acid was boiled under reflux and the change in optical rotation was observed at intervals. After 105 min. the xanthate group was obviously decomposing but the specific rotation of 22.5° was not far from the value of 13° roughly estimated for glucose-3-*S*-methyl xanthate from the molecular rotations of its monoisopropylidene derivative, of 1,2-*O*-isopropylidene glucose, and of glucose, in water or alcohol. The crude product when chromatographed yielded faint spots corresponding to glucose (R_f 0.20), to the isopropylidene methyl xanthate (R_f 0.92), and to an unknown substance. The major spot, with R_f 0.65, was attributed to the desired glucose-3-*S*-methyl xanthate. This compound partly decomposed when an attempt was made to free it from the associated glucose by a fermentation with yeast (16). A product whose purity was estimated from its sulphur content to be about 90% resulted when monoisopropylidene glucose methyl xanthate was boiled

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for two hours in 50% methanol containing 1% of sulphuric acid, which was then neutralized with barium carbonate. Some of the starting material, 54%, was recovered unchanged, and the crude glucose-3-*S*-methyl xanthate was isolated by evaporating the frozen aqueous liquor. The most satisfactory method of preparing glucose-3-*S*-methyl xanthate proved to be the partial hydrolysis of the more accessible diisopropylidene compound (I) in hot 80% acetic acid, which was used by Ness, Hann, and Hudson (12) in a similar case. Although 55% of the monoisopropylidene derivative was recovered, it was easy to eliminate the acetic acid and to purify the glucose-3-*S*-methyl xanthate by chromatography on a cellulose column. The product gave only a single spot of R_f 0.65 when chromatographed on paper, but nevertheless persisted as an uncrystallized, light yellow oil containing somewhat less than the calculated amount of sulphur.

The xanthation of methyl-4,6-*O*-benzylidene-α-D-glucoside was next undertaken. Although attempts to prepare the intermediate 2,3-di-sodio derivative with sodium in liquid ammonia according to Muskat (11) were not successful, the derivative apparently formed in high yield when a solution of the benzylidene compound in dioxane was mixed with a colloidal suspension of sodium in toluene. The subsequent addition of carbon disulphide to the suspension, followed still later by the addition of methyl iodide, produced crude, crystalline methyl 4,6-*O*-benzylidene-α-D-glucopyranoside-2,3-di-*S*-methyl xanthate (II) in about 70% yield. All attempts to remove the benzylidene group, or the benzylidene and methyl glucosidic groups, selectively led to yellow, evil-smelling oils containing less sulphur than the amounts expected for glucose-2,3-di-*S*-methyl xanthate or for the corresponding methyl glucoside. No single substance could be detected in these oils by the chromatographic methods used, and the attempt to prepare glucose-2,3-di-*S*-methyl xanthate was abandoned owing to the instability of the xanthate ester groups.

The most suitable compound from which to attempt a synthesis of glucose-6-*S*-methyl xanthate appeared to be the di-*O*-methylene glucose-6-acetate synthesized by Hough, Jones, and Magson (7), which was characterized as the 1,2;3,5-di-*O*-acetal by Schmidt, Distelmaier, and Reinhard (17) and later by Shyluk, Honeyman, and Timell (18). The replacement of the *O*-acetyl group by a sodium atom proceeded smoothly in alcoholic sodium hydroxide, and subsequent treatments with carbon disulphide and with methyl iodide produced the new, crystalline 1,2;3,5-di-*O*-methylene glucofuranose-6-*S*-methyl xanthate (III) in 84% yield. This compound was difficult to hydrolyze and the methylene and xanthate ester groups appeared to be removed at roughly the same rate. The most economic procedure found for the preparation of glucose-6-*S*-methyl xanthate was to boil a solution of the dimethylene derivative in 6% aqueous-alcoholic sulphuric acid for about three hours; about 80% of the starting material was recovered and recycled, and the hydrolyzates were accumulated. When these hydrolyzates were chromatographed on a cellulose column, a substance was isolated which had a single R_f value of 0.84 in the system used, and a sulphur content close to that required by glucose-6-*S*-methyl xanthate (S, 23.7%). All attempts to crystallize the

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product, or its tetraacetate, failed. In addition to glucose (R_f 0.13) the hydrolyzate contained a minor amount of a sirup containing 9.2% of sulphur and with an R_f value of 0.70. This sirup was presumably a decomposition product of the methyl xanthate, because the product from a similar hydrolysis prolonged for 68 hr., when chromatographed on paper, yielded the spot expected for glucose, and others with R_f values of 0.30, 0.56, and 0.70, the one at R_f 0.84 being absent.

Ness, Hann, and Hudson (13) showed that acetolysis replaced the methylene acetal rings in a trimethylene mannitol with acetyl and acetoxymethyl groups, while Lieser and Leckzyck (10) found that acetolysis at 0° did not affect a xanthate group. By combining the techniques used in these researches, it proved possible to cleave di-*O*-methylene-glucose-6-acetate to a presumed tri-*O*-acetyl-di-*O*-acetoxymethyl derivative and to deacetylate the latter to glucose. A repetition of the work with the xanthate ester (III) produced a sirup with the composition of a diacetyl diacetoxymethyl glucose methyl xanthate, but attempts to deacylate this substance, even with very mild conditions, resulted in some dexanthation. According to a paper chromatogram, the product contained a little glucose, much of the 6-*S*-methyl xanthate of R_f 0.84, and a little of the related substance of R_f 0.70.

The *S*-methyl xanthates (I), (II), and (III) were also hydrolyzed with cold concentrated hydrochloric acid in conditions suitable for the complete hydrolysis of a cellulose-*S*-methyl xanthate to the corresponding glucose derivatives. As expected, the 3-*S*-methyl xanthate group in (I) was completely removed and nothing but glucose was detected in the product; no substance was recognized in the hydrolyzate of the 2,3-di-*S*-methyl xanthate (II), but the 6-*S*-methyl xanthate (III) yielded 70% of a sirup containing glucose, glucose-6-*S*-methyl xanthate (R_f 0.84), and the derived substance of R_f 0.70. These experiments confirmed the observation that an *S*-methyl xanthate group located in the sixth position of glucose was much more stable toward acid than were those in the second and third positions.

EXPERIMENTAL

Analytical

Sulphur was determined according to Waters (21) by oxidizing 0.05 to 0.1 gm. samples with bromine – nitric acid and estimating the resulting sulphuric acid as the barium salt. Microdeterminations on 1–5 mgm. samples containing 10–20% sulphur were fairly accurate when the Grote combustion to sulphur dioxide was used, as described by Sundberg and Royer (19). The dioxide was oxidized by 3% aqueous hydrogen peroxide to sulphuric acid, which was increased in amount by the addition of exactly 10 ml. of 0.01 *N* acid before being titrated to exactly pH 5.5 with 0.004 *N* sodium hydroxide. The determination of acetyl groups by saponification (9) was inaccurate in presence of *S*-methyl xanthates, but Clark's saponification followed by steam-distillation (1) gave good results. The almost complete failure of the *S*-methyl xanthate group to yield methyl iodide (20) in a customary determination of alkoxyl groups (15) was confirmed.

Techniques used in paper chromatography were based on the description given by Partridge (14), butanol saturated with water being the solvent and ammoniacal silver nitrate usually being the spray.

*1,2;5,6-Di-O-isopropylidene-*D*-glucofuranose-3-S-methyl Xanthate* (*I*)

The 1,2;5,6-di-*O*-isopropylidene glucofuranose was prepared from glucose, acetone, anhydrous zinc chloride, and phosphoric acid as described by Glen, Myers, and Grant (5). After several recrystallizations, the melting point and specific rotation in water attained the correct values of 112–113° and $[\alpha]_D^{20}$ −18.8° (*c*, 2.04), respectively.

An excess of sodium in the form of thin plates was added in nine installments during 24 hr. to a solution of 50 gm. of diisopropylidene glucose in 200 ml. of dry ether kept under reflux on a steam bath. The ether solution was decanted and the residual sodium was washed three times with ether. The solution and washings containing the sodio-derivative were combined, cooled, mixed with 50 ml. of carbon disulphide, and kept at room temperature for 12 hr. The ether layer containing any unchanged diacetone glucose was then decanted, and the residual semisolid, cream-colored mass of crude xanthate salt was mixed with 15 ml. of pure methyl iodide. After being vigorously shaken at intervals during an hour to disintegrate the mass, the suspension was kept near 20° for six hours and was then filtered. The combined filtrate and washings were evaporated under nitrogen, and the solid residue was distilled at 150–160° and 0.6–0.7 mm. pressure. When a solution of the yellow distillate in ether was allowed to evaporate slowly, 61 gm. of crystals melting at 57–60° separated. This yield of the *S*-methyl xanthate amounted to 90% of theory, instead of 52% as reported by Freudenberg and Wolf (4). After recrystallization from petroleum ether the substance had the correct sulphur content, melted at 58–60°, and had a specific levo rotation of $[\alpha]_D^{22}$ −15.5° in chloroform (*c*, 2.00). The recorded values (4) were m.p. 61° and $[\alpha]_{5460}^{16}$ −14.6° in acetylene tetrachloride.

One gram of the crystalline methyl xanthate dissolved within five minutes when shaken at room temperature with 50 ml. of 37% hydrochloric acid. After six hours, when the solution had become dark red and developed an unpleasant odor, an equal volume of water was added. Six days later, and after further dilution with water, the acid was neutralized with basic lead carbonate and evaporated to dryness under diminished pressure. Extraction of the residue with five 25 ml. volumes of ethanol removed 0.5 gm. of a red sirup, which when chromatographed on paper gave a single spot corresponding to glucose.

*Mono-O-isopropylidene-*D*-glucofuranose-3-S-methyl Xanthate*

(*a*) A solution of 135 gm. of the diisopropylidene derivative in 140 ml. of absolute methanol containing 0.15% of anhydrous hydrogen chloride was heated under reflux for eight minutes. The solution was cooled, neutralized with basic lead carbonate, and filtered, lead being later removed as the sulphide from the filtrate. After being evaporated near 20° and under reduced pressure, the clear liquor left a residue which partly crystallized within two days. This

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residue was dissolved in hot ligroin (b.p. 80–110°) and the solution on cooling deposited 46 gm. (38.5%) of the product, m.p. 94–98°. Approximately 45 gm. (30%) of the unchanged diisopropylidene methyl xanthate was recovered from the mother liquor. A 3.3 gm. sample of the mono derivative when thrice recrystallized from 200 to 300 ml. of hot ligroin yielded 2 gm. of pure material melting at 101–102.5°. The specific levorotation was $[\alpha]_D^{24}$ −27.8° in chloroform (*c*, 2.00). Found: C, 42.5, 42.5; H, 5.9, 6.0; S, 20.7, 21.0%. Calc. for $C_{11}H_{18}O_6S_2$: C, 42.6; H, 5.8; S, 20.6%.

When a similar methanolysis of the diisopropylidene derivative was continued for about one hour, a 60–70% yield by weight was obtained of a white, evil-smelling, amorphous material which became liquid and discolored when exposed to the air. The substance was insoluble in ether but soluble in methanol. Found: S, 20.1; OCH_3, 2.8, 2.2%. The low value for apparent methoxyl made the formation of any methyl glycoside very doubtful.

Some of the crystalline monoisopropylidene glucose-*S*-methyl xanthate, 0.5 gm., was dissolved in 25 ml. of 0.05 *N* hydrochloric acid in aqueous ethanol (1 vol.: 1 vol.). Since the optical rotation as observed in a 2 dm. tube did not change within 12 hr. at room temperature, the solution was heated under reflux on a steam bath. After 0, 15, 30, 60, 75, and 105 min. the observed rotations corresponded to specific rotations of −27.5°, −12.5°, −3.8°, +5.0°, +7.5°, and +22.5°. The xanthate ester group was then decomposing, to judge from the odor and turbidity of the solution. The removal of hydrochloric acid from this solution by silver carbonate caused immediate blackening even at room temperature, and the use of Amberlite IR-4B anion exchange resin also removed half of the sulphur. The odor of mercaptan was strong when this resin was regenerated, first with alkali and then with acid. Basic lead carbonate was finally adopted as the neutralizing agent because no blackening occurred unless the solution was warmed. The lead was later removed as the sulphide, the clear filtrate was extracted with chloroform to recover most of the residual monoisopropylidene-glucose-*S*-methyl xanthate, and the aqueous phase was chromatographed on paper with the results already discussed.

(*b*) Following the method described by Ness, Hann, and Hudson (12), 2 gm. of diisopropylidene glucose-3-*S*-methyl xanthate was dissolved in 50 ml. of 80% acetic acid. The solution was heated under reflux for 30 min. in an oil bath kept at 120°, and was then evaporated to a sirup under reduced pressure. This sirup was extracted with 30 ml. of chloroform, and the dried extract on evaporation yielded 1.1 gm. (55%) of material which solidified on being stirred with ligroin. The solid, m.p. 75–88°, was shown by chromatographic methods to be the monoisopropylidene methyl xanthate contaminated with a small amount of the diisopropylidene derivative. The portion, 0.4 gm., of the above sirup which was insoluble in chloroform was saved (see below).

Glucose-3-S-methyl Xanthate

A solution of the above 0.4 gm. of sirup in 25 ml. of acetone was filtered, and a portion of the clear filtrate was chromatographed on paper. A small amount of glucose appeared to be present, together with a large amount of

the compound supposed to be glucose-3-*S*-methyl xanthate and a trace of a third substance of intermediate R_f value. An accumulation of 4.5 gm. of the sirup from several hydrolyses, and which had an average sulphur content of 20.45%, was then purified by passage through a cellulose column. The column was eluted with 1200 ml. of *n*-butanol saturated with water, and the eluate was collected in 21 fractions. Fractions Nos. 11 to 17 inclusive gave only one spot with an R_f value of 0.65 on a paper chromatogram. These fractions when combined and evaporated yielded 3 gm. of glucose-3-*S*-methyl xanthate as a light yellow sirup. Found: S, 20.1, 20.2%. Calc. for $C_8H_{14}O_6S_2$: S, 23.7%. The compound was not quite pure, and repeated attempts to crystallize it failed.

Methyl-4,6-O-benzylidene-α-D-glucopyranoside-2,3-di-S-methyl Xanthate

α-Methyl-D-glucoside and benzaldehyde were heated together as described by Irvine and Scott (8), and the resulting benzylidene derivative melted correctly at 163–164°. Eight grams of sodium, colloidally dispersed in 50% concentration in toluene, was added to a solution containing 8 gm. of methyl-4,6-benzylidene-α-D-glucoside in 50 ml. of dry, pure dioxane. The replacement of the dioxane by 800 ml. of dry benzene, or of the sodium by alcoholic sodium methylate followed by evaporation, was not successful. After being cooled in order to moderate the initial evolution of hydrogen, the suspension was kept warm on a steam bath for three hours, when a further 2 gm. of the dispersed sodium was added and heating was continued for eight hours. The suspension was then cooled, well mixed with 25 ml. of carbon disulphide, and kept overnight at room temperature to form the sodium xanthate. Methyl iodide, 9 ml., was added and after being kept for seven hours at room temperature the suspension was filtered free of sodium salts. The latter were washed three times with dry benzene, after which the filtrate and washings were evaporated under diminished pressure, finally in a desiccator. The red, viscous residue soon crystallized, yielding 9.2 gm. (72%) of crude methyl-4,6-*O*-benzylidene-α-D-glucoside-2,3-di-*S*-methyl xanthate melting at 65–84°. Two recrystallizations from 75% ethanol, followed by an extraction with ligroin and a recrystallization from 80% ethanol, left 4 gm. of the product as pure white crystals melting at 99–100.5°. The substance had a specific rotation of $[\alpha]_D^{22}$ −18.1° in chloroform (*c*, 1.66). Found: C, 46.9, 47.3; H, 4.7, 5.0; S, 27.3, 27.4%. Calc. for $C_{18}H_{22}O_6S_4$: C, 46.8; H, 4.8; S, 27.7%.

When chromatographed on paper, the dixanthate ester formed an intense spot near the solvent front. The parent substance, methyl benzylidene glucoside, left no record on this chromatogram. A 0.5 gm. sample of the dixanthate ester was then hydrolyzed with concentrated hydrochloric acid as described for the diisopropylidene glucose 3-*S*-methyl xanthate, and 0.23 gm. of an amorphous solid was recovered. Found: S, 10.3, 9.9%. When aniline phthalate was the spray, this solid produced no spot on a paper chromatogram, and presumably contained no glucose. Another hydrolysis involved heating a solution of 1 gm. of the dixanthate ester in a mixture of ethanol, 160 ml., water, 30 ml., and concentrated sulphuric acid, 6 ml., under reflux on the steam bath for two hours. After neutralization to pH 6 and complete evapo-

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ration, the liquor yielded salts and 0.3 gm. of a yellow sirup soluble in chloroform. Found: S, 16.0, 16.1%. This sirup when chromatographed on paper gave one spot of R_f 0.87, ammoniacal silver nitrate being the spray. No spot was developed with an aniline phthalate spray, as was the case when substituted glucose-3 and 6-*S*-methyl xanthates were hydrolyzed.

*1,2;3,5-Di-O-methylene-α-*D*-glucofuranose-6-S-methyl Xanthate*

The procedure of Hough, Jones, and Magson (7) was used to prepare the corresponding 6-acetate from glucose, 162 gm., paraformaldehyde, 165 gm., glacial acetic acid, 500 ml., and concentrated sulphuric acid, 75 ml. The crude, partly crystallized product, 83 gm. (37%), on recrystallization from methanol yielded 32 gm. of pure material melting correctly at 103–105°.

Five grams of sodium hydroxide, 25 gm. of the bismethylene-6-*O*-acetylglucose, and 50 ml. of absolute ethanol were shaken together until the bismethylene derivative went completely into solution owing to deacetylation. Water, 10–15 ml., was then added to dissolve the residual sodium hydroxide and two hours later the yellow solution was evaporated to dryness *in vacuo*, finally by the addition and evaporation of 25 ml. of benzene. The bismethylene glucose was extracted from this residue by dry benzene, 100 ml., boiling under reflux, and after the extract had cooled it was mixed with an excess of sodium colloidally dispersed in 25 ml. of dry benzene. After the initial reaction had subsided, 2 gm. of sodium dispersed in toluene was added, together with 25 ml. of benzene. The mixture was kept next day near 75° for four hours, cooled, and shaken with 25 ml. of carbon disulphide. The following day, when the formation of the sodium xanthate was judged to be complete, 30 ml. of methyl iodide was added to the suspension. After being shaken occasionally during a few hours, the suspension was filtered and the residual salts were washed three times with 25 ml. volumes of benzene. Evaporation of the filtrate and washings yielded 32 gm. (108%) of crude product melting at 77–88°, increased to 97–99° by recrystallization from 500 ml. of 70% ethanol followed by extraction with low-boiling ligroin. The yield of pure white needles was 25.1 gm., or 84%, and the specific rotation, $[\alpha]_D^{21}$ +27.3° in chloroform (*c*, 2.15). Found: C, 40.8, 41.1; H, 5.0, 5.1; S, 21.3, 21.7%. Calc. for $C_{10}H_{14}O_6S_2$: C, 40.8; H, 4.8; S, 21.8%.

A 1-gm. sample was hydrolyzed in concentrated hydrochloric acid as described for the diisopropylidene-3-*S*-methyl xanthate. A residue, 0.1 gm., (m.p. 81–92°) failed to dissolve within six hours and was removed. The cream-colored solution was then diluted with an equal volume of water and kept for six days, when the color had deepened only to light yellow. After being neutralized, this solution was evaporated to dryness, and an alcoholic extract of the residue yielded 0.7 gm. of a yellow sirup when evaporated in a desiccator. A portion of this sirup when chromatographed on paper, using an aniline phthalate spray, yielded a faint spot corresponding to glucose, and two major spots (R_f 0.84 and 0.70, see below) corresponding to glucose-6-*S*-methyl xanthate.

Glucose-6-S-methyl Xanthate

One gram of the pure bismethylene derivative was boiled under reflux after

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solution in 150 ml. of a mixture made up from absolute ethanol, 160 ml., water, 30 ml., and concentrated sulphuric acid, 6 ml. Although some of the xanthate survived when the solution was boiled for 68 hr., more was hydrolyzed to glucose or was decomposed, and the time was restricted to 165 min. The solution was evaporated near 35° to 10 ml., and was diluted with 100 ml. of water to precipitate 0.8 gm. of unchanged bismethylene derivative (m.p. 91–96°). After neutralization with barium carbonate and filtration, the filtrate on evaporation yielded 0.15 gm. (17%) of a sirup. An accumulation of such sirups from several hydrolyses was extracted with acetone, and 2 gm. of an oil was recovered from the extract. This oil was eluted from a cellulose column with a total of 1400 ml. of *n*-butanol saturated with water. Of the 34 fractions of eluate collected, Nos. 2 to 8 inclusive yielded a single spot of R_f 0.84 when chromatographed on paper, with ammoniacal silver nitrate as the spray. When these fractions were combined and evaporated, 1.1 gm. of crude glucose-6-*S*-methyl xanthate remained as a yellow sirup which could not be crystallized. Found: S, 20.7, 21.4%. Calc. for $C_8H_{14}O_6S_2$: S, 23.7%. Fractions Nos. 22 to 26 inclusive when chromatographed on paper each yielded a single spot of R_f 0.71; these fractions together gave 70 mgm. of a sirup whose nature was not determined. Found: S, 9.1, 9.3%.

The supposed glucose-6-*S*-methyl xanthate, 0.65 gm. (R_f 0.84), was acetylated with 20 ml. of acetic anhydride containing 0.4 gm. of anhydrous zinc chloride for 24 hr. at room temperature. The solution was poured into ice and water, the mixture was neutralized and extracted with ether. Evaporation of the extract left a yellow sirup which was dried in a vacuum desiccator over phosphorus pentoxide. Yield 0.9 gm. or 85%. Found: S, 12.2, 12.5; acetyl, 38.0, 38.1%. Calc. for 1,2,3,4-tetra-*O*-acetyl glucopyranose-6-*S*-methyl xanthate: $C_{16}H_{22}O_{10}S_2$: S, 14.6; acetyl, 39.3%.

Acetolysis of Bismethylene-glucose-6-S-methyl Xanthate

Anhydrous zinc chloride, 0.1 gm., was added to a solution of 1 gm. of the pure xanthate ester in 5 ml. of acetic anhydride. The mixture was warmed on a steam bath and shaken occasionally until the zinc chloride completely dissolved. After being left at room temperature for 16 hr., the product was precipitated by pouring the solution into ice and water. A yellow sirup, presumably a diacetyl diacetoxymethyl glucose-6-*S*-methyl xanthate, was obtained. Yield 1.6 gm. or 90%. Found: C, 42.9, 42.9; H, 5.0, 5.2; S, 12.7, 12.0%. Calc. for $C_{18}H_{26}O_{12}S_2$: C, 43.4; H, 5.2; S, 12.8%.

In order to deacetylate the above product, an accumulation of 5.2 gm. was dissolved in 100 ml. of absolute methanol, and a total of 2 ml. of 1.5 *N* barium methylate in methanol was added at intervals to maintain the pH between 7.0 and 7.5 for four days (23). The pH was then adjusted to 5.5 with dilute sulphuric acid, and the filtrate from the precipitated barium sulphate was cautiously evaporated to a sirup weighing 2.2 gm. (70%). The pungent smell of formaldehyde was evident during this evaporation. A paper chromatogram of this sirup showed that it contained a little glucose, while an intense spot at R_f 0.84 and a light one at R_f 0.70 suggested the presence of much glucose-

6-S-methyl xanthate. Aniline phthalate was the spray. No recognizable product was obtained when the deacetylation was carried out by Kunz and Hudson's method (9) employing 0.1 *N* sodium hydroxide in aqueous acetone at $-10°$.

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PHOSPHORYLETHANOLAMINE[1]

By Erich Baer and Harvey C. Stancer

ABSTRACT

A synthetic procedure is described that gives in excellent yield pure phosphorylethanolamine. Its X-ray diffraction pattern and infrared spectrum are reported.

Phosphorylethanolamine (PE) occurs in biological materials both in the bound and in the free state. The isolation of PE from malignant tumors by Outhouse (17), working with E. J. King in the Banting and Best Department, supplied the first evidence for the existence of free PE in nature. Subsequently it was also found in the intestines of rats and rabbits (13), in calf embryo muscle (15), in brain (2, 3, 22), and in various tissues of cows (24). Phosphorylethanolamine has been obtained by synthesis in yields ranging from 20% to 67%: (*a*) by phosphorylation of ethanolamine phosphate (17) or ethanolamine (19) with phosphorus oxychloride, (*b*) by phosphorylation of ethanolamine with a mixture of phosphorus pentoxide and phosphoric acid (19), (*c*) by treatment of phosphorylchloroethanol with ammonia (19), and (*d*) by the interaction of orthophosphoric acid and ethylenimine (11). The widely differing melting points reported for PE (228° (19), 230° (17), 232°–233° (19), 240° (11), and 244° (18, 12)) indicate, however, that these procedures give mixtures of organic phosphates from which it is apparently difficult to obtain the pure substance. In view of the biological interest that phosphorylethanolamine possesses it seemed desirable to develop a procedure for its synthesis that would give in good yield pure phosphorylethanolamine. This has been accomplished by substituting N-carbobenzoxyethanolamine for ethanolamine, and using diphenylphosphoryl chloride instead of phosphorus oxychloride as phosphorylating agent, thus preventing the formation of any by-product. The resulting O-diphenylphosphoryl carbobenzoxyethanolamine is freed of its protective benzyl and phenyl groups by consecutive catalytic hydrogenolysis with palladium in ethanol, and platinum in acetic acid, respectively. This procedure gives a chromatographically pure, crystalline phosphorylethanolamine in an over-all yield of 83%. Its melting point (244°–245°) agrees well with that reported by Outhouse (18) and Clarke *et al.* (12) for phosphorylethanolamine.

Attempts to simplify our procedure by removing the phenyl and carbobenzoxy groups by hydrolysis in boiling barium hydroxide solution were not successful, although the same procedure when applied to diphenylphosphorylcholine chloride (4) gives in good yield the barium salt of phosphorylcholine chloride. The protective carbobenzoxy group can be removed selectively, however, by the method of Albertson and McKay (1), using gaseous hydrogen bromide. The O-diphenylphosphorylethanolamine hydrobromide is obtained in a yield of approximately 90%. Since this compound might prove useful as a

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Contribution from the Banting and Best Department of Medical Research, University of Toronto, Toronto, Ontario.

substrate in studies with phosphatases, its preparation is described in the experimental part.

In order to facilitate both the study of the structure and the quantitative estimation of natural phosphatides by infrared spectroscopy (14, 16, 21), the infrared spectra of pure individual phosphatides have been reported from this laboratory as these substances became available by synthesis (5, 6, 7). Possessing analytically pure specimens of phosphorylethanolamine and L-α-glycerylphosphorylethanolamine (8), both of which are of interest as moieties of cephalins and plasmalogens, their infrared spectra were recorded; these are shown in Fig. 1.

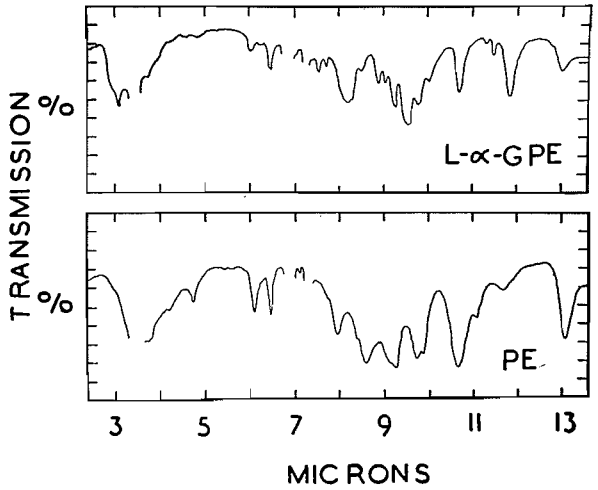
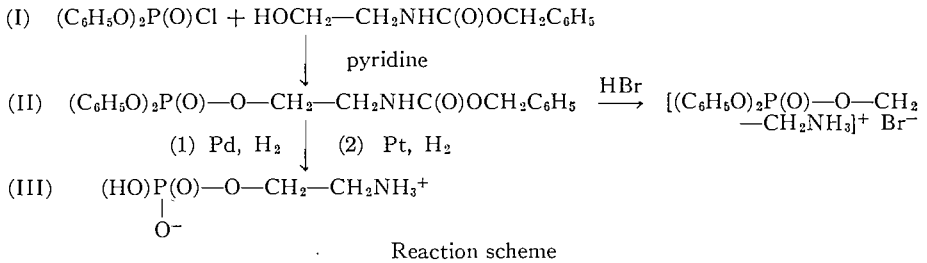


FIG. 1. Infrared spectra of phosphorylethanolamine (PE) and L-α-glycerylphosphorylethanolamine (GPE) in nujol mulls. Perkin-Elmer double-beam infrared spectrophotometer (model 21). Potassium bromide prism. Band positions and probable assignments: (PE) 2.90 μ (OH and NH stretching), 4.73, 6.08, 6.44 (NH bending), 7.10 (CH, OH bending), 7.94 (OH bending, P=O), 8.60 (C—O, C—N, C—C stretching), 9.25 (covalent phosphate), 9.72, 9.85, 10.64 (covalent phosphate), 11.08, 11.66, 13.08. (GPE) 3.10 μ (NH and OH stretching), 6.02, 6.48 (NH bending), 7.56 (CH, OH bending; primary and secondary alcohols), 7.74 (CH, OH bending; P=O), 8.18 (covalent phosphate), 8.55 (C—O, C—N, C—C stretching), 8.92, 9.08, and 9.30 (covalent phosphate), 9.58, 9.82, 10.06, 10.76 (covalent phosphate), 11.36, 11.52, 11.88, 13.06.



Reaction scheme

EXPERIMENTAL PART

O-(Diphenylphosphoryl)-carbobenzoxyethanolamine

To a solution of 9.75 gm. (5.0 mM.) of N-carbobenzoxyethanolamine (10,

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20) in 40 ml. (50 mM.) of anhydrous pyridine* was added with swirling and under anhydrous conditions 14.8 gm. (5.5 mM.) of diphenylphosphoryl chloride (9) over a period of 10 min. To prevent the temperature from rising above 40°, the mixture was cooled occasionally with cold water. After it had been left for two hours at room temperature, the excess of diphenylphosphoryl chloride was destroyed by the addition of 2 ml. of water. One hour later the reaction product was isolated by precipitating it with 300 ml. of water. It was purified by washing its solution in 175 ml. of ether in succession with two 25 ml. portions of ice-cold 5 *N* sulphuric acid, and one 25 ml. portion each of water, a half-saturated solution of sodium bicarbonate, and water. After the solution had been dried over anhydrous sodium sulphate, it was concentrated under reduced pressure and the remaining solvent was removed by keeping the substance at 30°–35° in a vacuum of less than 1 mm. Hg for a period of five hours. The O-diphenylphosphoryl carbobenzoxyethanolamine, an almost colorless oil, weighed 20.4 gm. (95.4% of the theoretical amount based on carbobenzoxyethanolamine) $n_D^{23°}$ 1.5555. The substance is readily soluble at room temperature in ether, ethanol, methanol, or acetic acid but is insoluble in water. $C_{22}H_{22}O_6NP$ (427.2). Calculated: C, 61.81; H, 5.19; N, 3.29; P, 7.25. Found:† C, 61.79; H, 5.16; N, 3.30, 3.25; P, 7.12, 7.23.

Phosphorylethanolamine

A solution of 21.3 gm. (50 mM.) of O-diphenylphosphoryl carbobenzoxyethanolamine in 200 ml. of 99% ethanol together with 3.5 gm. of palladium catalyst (23) was shaken vigorously in an all-glass hydrogenation vessel of approximately 1 liter capacity in an atmosphere of pure hydrogen under a pressure of 40–50 cm. of water until the absorption of hydrogen had practically ceased. After replacing the hydrogen with nitrogen and adding 75 ml. of water to dissolve the reaction product, the catalyst was removed and the solution was brought to dryness under reduced pressure at a bath temperature of 25°–35°. To complete the removal of the protective groups, the solid residue was dissolved in 175 ml. of glacial acetic acid and the solution, after it was returned to the hydrogenation vessel and 3.5 gm. of platinic oxide‡ (Adams' catalyst) added, was shaken until there was no further uptake of hydrogen. After replacing the hydrogen with nitrogen and removing the catalyst, the acetic acid was distilled off *in vacuo* (bath temperature 30°–35°). The crude phosphorylethanolamine, containing traces of potassium, was purified by dissolving it in 350 ml. of distilled water and shaking the solution with 35 gm. of Amberlite IR–120 (H) for 90 min. The filtrate was brought to dryness *in vacuo* (bath temperature 30°–35°) and the phosphorylethanolamine was recrystallized from 35 ml. of water by gradually adding several volumes of 99% ethanol, and placing the mixture in an ice-box. The crystals were filtered off, washed with a small amount of a cold mixture of

*Pyridine of good commercial grade was refluxed over barium oxide and distilled with the exclusion of moisture.

†Analyses of two independent preparations.

‡The catalyst was prepared as described in "Organic Syntheses", Coll. Vol. 1, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 463, with the exception that the sodium nitrate was replaced by an equimolecular amount of potassium nitrate.

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ethanol and water (2:1), and dried *in vacuo* over phosphorus pentoxide. The phosphorylethanolamine weighed 6.0 gm. (87% of theory). Over-all yield 83%, m.p. 244°–245°.* $C_2H_8O_4NP$ (141.1). Calculated: C, 17.02; H, 5.71; N, 9.93; P, 22.0. Found: C, 17.10; H, 5.60; N, 9.88; P, 22.0.

X-ray Diffraction Pattern of Phosphorylethanolamine

The X-ray powder diffraction pattern was taken using Ni-filtered Cu K_α-radiation (λ 1.5418). The intensities of the diffraction rings were estimated visually on an arbitrary scale of 1 to 10 and are quoted in parentheses:
8.85 Å ($\frac{1}{2}$), 5.77 (7), 5.17 (4), 4.41 (10), 4.26 (10), 3.88 (8), 3.84 (8), 3.76 ($\frac{1}{2}$), 3.58 (5), 3.48 ($\frac{1}{2}$), 3.28 ($\frac{1}{2}$), 2.91 (1), 2.87 ($\frac{1}{2}$), 2.71 (3), 2.63 (2), 2.47 (3), 2.42 (1), 2.22 (3).

Diphenylphosphorylethanolamine Hydrobromide

Through a solution of 3.0 gm. of O-diphenylphosphoryl carbobenzoxyethanolamine in 20 ml. of glacial acetic acid was passed a stream of hydrogen bromide† gas for one-half hour. The solution was occasionally cooled. After the solution was left for one-half hour at room temperature, the solvent and excess of hydrobromide were removed under reduced pressure (8–10 mm. Hg) at a bath temperature of 35°–40°. To the solution of the residual oil in 5 ml. of 99% ethanol, ether was added until the solution was permanently turbid, and the mixture was placed in an ice-box overnight. The crystalline diphenylphosphorylethanolamine hydrobromide was collected with suction on a buchner funnel and was dried *in vacuo* over paraffin and calcium chloride. Yield 2.32 gm. (88% of theory), m.p. 115°–116.5° (with slight sintering at 114°). $C_{14}H_{17}O_4NPBr$ (374.2). Calculated: C, 44.93; H, 4.58; N, 3.74; P, 8.28. Found:‡ C, 44.96, 45.27; H, 4.75, 4.65; N, 3.79; P, 8.32.

This work was supported by a grant from the Lipotropic Research Fund, New York, to which the authors wish to express their sincere thanks. The authors express their thanks also to Professor E. W. Nuffield (Department of Geological Sciences, University of Toronto) for the X-ray diffraction measurements of phosphorylethanolamine, and to Dr. M. Look (Stanford University) for the infrared absorption spectra of phosphorylethanolamine and glycerylphosphorylethanolamine.

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**All melting points were determined in capillary tubes using an electrically heated bath of n-butyl phthalate and short-stem thermometers with a range of 50°.*
†The gaseous hydrogen bromide was prepared by the action of bromine on tetrahydronaphthalene.
‡Analyses of two independent preparations.

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A SEARCH FOR THE CHEMICAL EFFECTS OF INTERNAL CONVERSION FOLLOWING RADIATIVE NEUTRON CAPTURE[1]

By A. G. Maddock and M. M. de Maine[2]

ABSTRACT

The possibility that neutron capture would lead to oxidation, because of internal conversion of the capture radiation, has been investigated in solid compounds of the lower valence states of antimony, arsenic, cerium, chromium, and thallium. Except in the hydrated compounds, negative results have been obtained. It is possible that oxidation is followed by electron-transfer exchange in the irradiated solids.

INTRODUCTION

When an atom captures a thermal neutron, there results a highly excited compound nucleus which quickly radiates its excess energy in one or more gamma-rays. Conservation of momentum requires that the emission of these gamma-rays imparts to the newly formed atom a recoil energy many times that required for breaking chemical bonds. It is also possible that one or more of the gamma-rays might be internally converted and in this instance, oxidation of the atom will result. Most studies on the chemical changes following thermal neutron capture have focused on the bond breaking mechanisms, but there could be oxidation effects due to internal conversion, even if simple ionic solids were irradiated (10).

The physical detection of internal conversion following radiative neutron capture is attended with some experimental difficulties; but with a 180° beta-ray spectrograph Hibdon and Muehlhause (7) have detected the conversion electrons from neutron capture in $_{48}Cd^{113}$, $_{66}Dy^{164}$, $_{64}Gd^{odd}$, $_{88}Hg^{199}$, and $_{62}Sm^{149}$. Thermal neutron irradiation of ethyl bromide and iodide at pressures of three microns leads to 12 to 50% of the radioactive atoms of the different isotopes becoming positively charged as a result of internal conversion (16). Most of the gold and iridium recoil atoms which escape from the surface of gold and iridium films during neutron irradiation are positively charged (12, 19).

It seemed possible that chemical methods might provide a more sensitive means of detection and estimation of the internal conversion. Radioactive perrhenate has been separated after dissolution of neutron-irradiated rhenium trichloride (6). Following the neutron irradiation of several hydrated chromic salts, 3 to 10% of the radioactive chromium atoms were found in the hexavalent state upon solution and analysis of the crystals (4).

EXPERIMENTAL

In the present work, neutron irradiation of several simple inorganic salts with the cation in the lower of its two stable chemical valences was followed by dissolution of the solids in solutions containing as carriers cations of both valence states. There followed a chemical separation of the cations by a method

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Contribution from the University Chemical Laboratory, Pembroke Street, Cambridge, England.
[2]*Lately Miss M. M. Moodie.*

which was chosen to avoid exchange between the two valence states. Measurements of the fraction of the radioactivity associated with each of the valence states were made. It was hoped that these would indicate the fraction of events leading to internal conversion and a consequent valence increase. Table I gives the present results together with those of Harbottle (4) for the hydrated chromic salts.

TABLE I

PERCENTAGE VALUES OF ATOMS PASSING INTO HIGHER VALENCE STATES DURING THE CONTROL ANALYSIS AND AFTER THERMAL NEUTRON IRRADIATION AND ANALYSIS
The values denoted* are those obtained by Harbottle (4)

Compound irradiated	Percentage of atoms in higher valence after irradiation and analysis		Percentage of atoms passing into higher valence during control analysis
Sb_2O_3	Sb^{122}	0.4	0.6
	Sb^{124}	0.4	
$KSbC_4H_4O_7.\frac{1}{2}H_2O$	Sb^{122}	1.8	
	Sb^{124}	1.8	
As_2O_3	1.0		1.1
$Ce_2(SO_4)_3$	Ce^{141}	2.0	2.0
	Ce^{143}	2.0	
$CrCl_3.10H_2O$	1.1		1.2
$Cr_2(SO_4)_3.18H_2O$	2.9		
$Cr_2(SO_4)_3.18H_2O$*	3.7		
$Cr(NO_3)_3.9H_2O$*	7.6		
$Cr_2(SO_4)_3.K_2SO_4.24H_2O$*	8.4		
$Cr_2(SO_4)_3(NH_4)_2SO_4.24H_2O$*	9.8		
Tl_2CO_3	0.9		0.9
$TlNO_3$	0.9		
Tl_2SO_4	0.9		

The methods of analysis for compounds of the different cations are as follows:

Antimony.—A magnesium chloride – hydrochloric acid solution of the irradiated compound with inactive Sb^{+3} and Sb^{+5} carriers was shaken with isopropyl ether which extracted the pentavalent antimony (2).

Arsenic.—The arsenate was separated from arsenite by precipitation of magnesium ammonium arsenite according to the procedures of Wilson and Dickinson (18).

Cerium.—Ceric compounds were extracted from cerous compounds by the use of ether after solution in nitric acid (8).

Chromium.—In one aliquot chromate was precipitated on the addition of lead nitrate solution. A second aliquot was treated with sodium hydroxide – sodium peroxide to oxidize chromic ions to chromate, and the lead chromate was then precipitated (3).

Thallium.—Thallous chromate was precipitated from the first aliquot. Sodium bisulphite treatment of a second aliquot reduced thallic ions to thallous, and the total thallium was precipitated as thallous chromate (5, 14).

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DISCUSSION

Negative results were obtained except where hydrated compounds were used. In these cases very strongly oxidizing species might be formed by the action of the ionizing radiations on the water. The same remarks apply to aqueous solutions in which oxidizing effects have also been revealed (13). Positive effects in anhydrous compounds are necessary if it is to be argued that internal conversion is responsible.

Unfortunately these negative results do not prove that internal conversion does not take place. Indeed, the physical investigations (7) suggest that it is sufficiently commonplace to have occurred in one or more of these isotopes. The detection method used is only valid if exchange by electron transfer does not take place in the solid or during dissolution. The control tests only show that it does not interfere after dissolution.

Very little evidence is available concerning exchange in solid systems. The phenomenon of induced exchange during precipitation is widely recognized (15), but it has not been investigated systematically. In fact, it is difficult to obtain reproducibility in such measurements. Nevertheless, the existence of this phenomenon suggests that exchange might take place during the solution of solids containing atoms in two valence states.

In a number of solids, containing different valences of one element, physical evidence such as the optical and electrical properties suggests that some delocalization of valence electrons takes place. Such a process might be expected to lead to exchange by electron transfer. In some cases a similar interaction of atoms in two valence states can occur in solution (9, 17).

However, exchange is not inevitable even when interaction between the atoms seems to occur. Thus the deep orange lead sesquioxide can be prepared and decomposed without exchange taking place (20). Similar results have been obtained with chromic chromate (1, 11). This latter result suggests that exchange need not occur, at least in oxygenated chromic compounds. Such salts are all hydrated, however.

Even the absence of exchange during precipitation and subsequent dissolution of the compounds studied does not preclude electron transfer within the solid lattice. The radioactive atom suffers a considerable recoil and frequently settles down in some interstitial or other abnormal lattice position. Nothing is known about the probability of electron transfer involving such atoms, but it is probably enhanced.

The previous observation on rhenium trichloride (6) seems all the more surprising in the light of these results.

One of us (M.M.M.) is indebted to the Royal Commission for the Exhibition of 1851 for a Science Overseas Scholarship which made possible her sojourn in Cambridge.

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INFLUENCE OF METHANOL ON VISCOSITY AND LIGHT SCATTERING PROPERTIES OF DEXTRAN SOLUTIONS[1]

By W. Donald Graham, Odette Patry, and E. Helen Jackman

ABSTRACT

Failure to consider the presence of up to 16% by volume of methanol in solutions of dextran fractions had a very marked effect on *apparent* intrinsic viscosity determinations (the term *apparent* signifies that measurements were made assuming that the solvent was water only). Unless methanol were removed or otherwise taken into account, high erroneous results were obtained. *Apparent* weight average molecular weights determined by light scattering were not significantly affected at these alcohol concentrations. The relations found over the range 0 to 16% methanol for dextran samples with weight average molecular weights of 265,000, 155,000, and 72,000 held for the latter sample up to 44% methanol. In the higher range of alcohol concentration the *apparent* weight average molecular weight was depressed. The true intrinsic viscosity of dextran solutions decreased as methanol concentration was increased.

During the course of testing dextran plasma expanders for conformity with various specifications, fractions representing the upper and lower 5 to 10% of the molecular weight distribution of the polymer are separated, usually by fractional precipitation with methanol. In some procedures no definite recommendation is made to ensure removal of traces of methanol which may remain with the precipitated dextran. According to Wolff *et al.* (8) this sirupy residue may contain up to 15% of methanol. Where great care in the separation of the supernatant solution from the viscous dextran-bearing precipitate is not exercised, it may be appreciated that variable and quite significant amounts of methanol may find their way into the test solution. In practice, when sharp separation of the layers is recognized as essential, the concentration of methanol in the final test solution (approximately 1 to 2% dextran in 100 ml. of solution) would be unlikely to exceed 2%. If test fractions are freeze-dried before they are dissolved for viscosity determinations etc., the methanol content should be of no practical significance.

Some laboratories have used light scattering measurements to assess the weight average molecular weights of these high and low fractions directly: others have made intrinsic or inherent viscosity determinations and converted the values thus obtained to "weight average molecular weights" by the application of a mathematical relationship (2, 3, 4, 6). The question arose as to the possible effects of varying amounts of methanol in the solutions on the subsequent molecular weight determinations. In an attempt to answer this question the present investigation was undertaken.

It was considered that the presence of methanol might have a greater effect on high molecular weight fractions than on low molecular weight material since larger dextran molecules tend to precipitate at lower concentra-

[1]*Manuscript received December 5, 1955.*
Contribution from the Food and Drug Laboratories, Department of National Health and Welfare, Ottawa, Canada.

tions of methanol. Accordingly three dextrans with weight average molecular weights of approximately 265,000, 155,000, and 72,000 respectively were selected for this study.

EXPERIMENTAL AND RESULTS

Approximately 2.0% solutions of these dextrans were prepared in essentially dust-free, glass-distilled water and to 50 ml. aliquots of these solutions, varying amounts of methanol (B.P.C. grade, absolute) from 0 through 16 ml. were added. Sufficient water was added to bring each solution to 100 ml. These solutions were intended to represent dextran fractions which were obtained by methanol precipitation and in which varying amounts of contaminating methanol were present. From each of these solutions four dilutions were prepared in essentially dust-free water to contain approximately 0.15, 0.2, 0.25, and 0.35 gm. of dextran/50 ml. These dilutions were clarified by filtration through an ultrafine, sintered glass, pressure filter so that the dissymmetry of the filtered solutions in the Brice-Phoenix light scattering photometer, series 1000, was not greater than 1.15 at λ 436 mμ. It was noted that filtration became progressively slower as the amount of methanol present increased and the filters required frequent cleaning with hot nitric and sulphuric acid (1:1). The absolute turbidities of the solutions were measured and the solutions were reserved for polarimetric and viscosity measurements. Turbidities were corrected for the turbidity of the solvent* and the expression Hc/τ† was calculated for each dilution. From the Hc/τ vs. c data the intercept at $c = 0$ was calculated by least squares and the reciprocal of this intercept was recorded as the *apparent* weight average molecular weight.

No attempt was made to allow for the fact that measurements were made in a three-component system as no such correction would be made by the analyst who ignored or was unaware of the presence of methanol in his solutions. For the same reason, in the determination of the viscosities of these solutions as described below, the solvent was considered to be water rather than water–methanol mixtures.

The viscosities of the four dilutions were determined using Ostwald-Cannon-Fenske viscosity pipettes (1) series 50, all of which had flow times with water at 25°C. in excess of 240 sec. Duplicate determinations were required to check within 0.3 sec. The viscosity data were converted to *apparent* relative viscosities and thence to *apparent* specific viscosities (*app.* η_{sp}). The *app.* η_{sp}/c vs. c data were utilized in the least squares calculation of the intercept at $c = 0$ which was recorded as *apparent* intrinsic viscosity (*app.* $[\eta]$). Concentrations of the solutions under test were determined polarimetrically in a Rudolph precision photoelectric polarimeter assuming $[\alpha]_D^{20} = +200°$. The effect of methanol was ignored since it has been shown by Snyder *et al.* (5) that the specific rotation is increased by only about 1% by the presence of 40% methanol by volume. The data arising from the viscosity and light scattering measurements are recorded graphically in Fig. 1.

*Turbidities of the aqueous methanol solutions were not greatly different from that of water which commonly was 4 to 5 × 10^{-5} cm.$^{-1}$.

†$H = 0.624 \times 10^{-5}$, c = concentration in gm./ml., τ = turbidity in cm.$^{-1}$.

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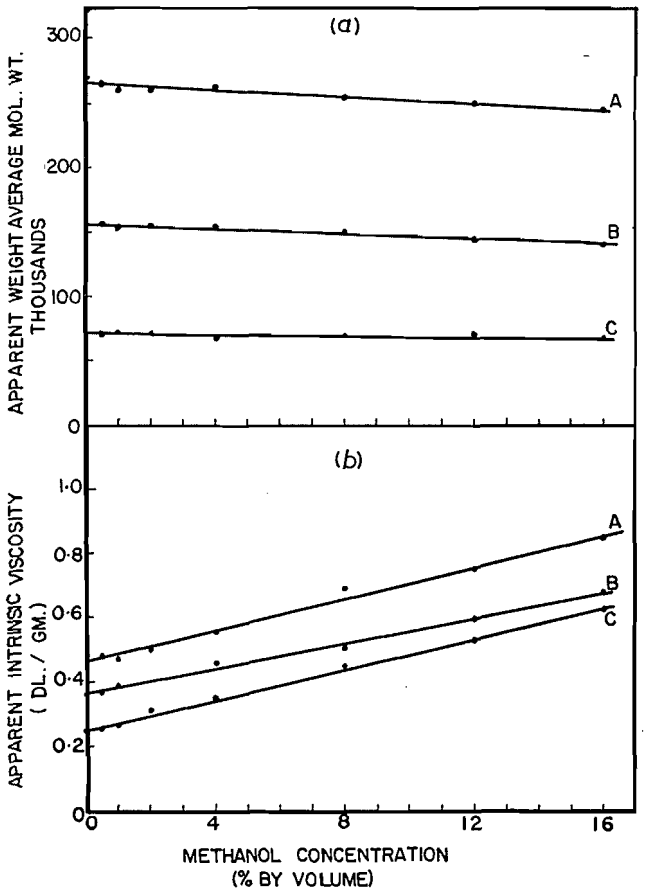

FIG. 1. Effect of methanol on (*a*) light scattering and (*b*) viscosity measurements on dextran solutions. Curve A—dextran sample 1, wt. av. mol. wt. 72,000; Curve B—dextran sample 2, wt. av. mol. wt. 155,000; Curve C—dextran sample 3, wt. av. mol. wt. 265,000.

It is obvious that the presence of amounts of methanol up to 16% by volume in the original dextran solution had relatively little effect on the *apparent* weight average molecular weight as determined by light scattering. The slight decrease in *apparent* weight average molecular weight with increasing methanol concentration is within the limits of reproducibility of the method (2) although the consistent trend suggests (*a*) increasingly serious loss of the larger molecules with increasing methanol concentration during filtration, (*b*) an error associated with ignoring the effects of the third component in the system, or (*c*) a combination of (*a*) and (*b*). Support for the first of these is found in the increasingly difficult filtration with increasing methanol concentration, particularly with the higher molecular weight dextran. The effect of the methanol *per se* might be expected to be small because the refractive index for aqueous methanol solutions in this concentration range is close to that of water (7). The gradual decrease in apparent molecular weight was associated with a small decrease in the second virial coefficients as the methanol concentration increased.

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Light scattering measurements on sample 3 were extended up to methanol concentrations of 44%. The initial trend, apparent in Fig. 1(*a*) curve C, was continued and, at a methanol concentration of 44% in the starting dextran solution, the *apparent* weight average molecular weight was further depressed to about 64,000 from the initial 72,000 measured in water. This would appear to be a significant degree of depression (2).

In the case of *apparent* intrinsic viscosity, Fig. 1(*b*), the values obtained ignoring the presence of methanol rose very steeply as the methanol concentration increased. While it is unlikely that methanol concentrations in the dextran fraction solutions, as obtained in practice, would reach 16%, measurements on sample 3 were extended up to the point of incipient precipitation at 44% methanol. The curve continued upward with the same trend shown in the lower ranges in curve C, Fig. 1(*b*).

In Fig. 2 have been plotted (curve A) the *apparent* relative viscosities of solutions containing 0.5% of dextran sample 3 and increasing amounts of methanol. The *apparent* relative viscosities were obtained by dividing

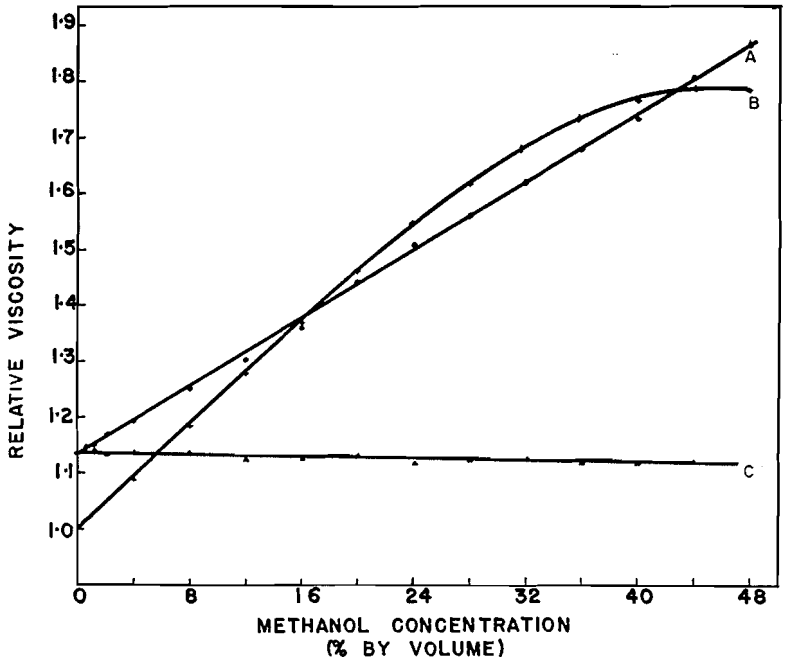

FIG. 2. Relative viscosities. Curve A—*Apparent* relative viscosity of a 0.5% solution of dextran sample 3 in the presence of increasing amounts of methanol. See text. Curve B—Relative viscosity of methanol solutions 0 to 48% by volume at 25°C. Curve C—Relative viscosities of solutions containing 0.5% of dextran sample 3 and varying amounts of methanol up to 44% by volume.

$\eta_{solution}$ by η_{water} ignoring the presence of methanol. The correction applied for density of the solutions was that applicable to dextran in water. In the same figure are plotted the true relative viscosities for aqueous methanol solutions with and without dextran (0.5% of sample 3) over the same range of methanol

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concentrations (curves C and B respectively). Since the viscosities of water–methanol mixtures show a maximum for intermediate compositions, the increase in viscosity with increasing methanol content can be attributed to the solvent viscosity.

When appropriate aqueous methanol solutions are used to determine $\eta_{solvent}$, and the true $\eta_{relative}$ for each dextran dilution is determined, the η_{sp}/c may be calculated for each dilution. From these figures, by least squares extrapolation to $c = 0$, a value related to intrinsic viscosity may be obtained. Starting with the usual 1% dextran solutions containing increasing amounts of methanol up to 44% by volume, curve A shown in Fig. 3 was obtained for sample 3. Corrections for density were applied in the viscosity determinations.

It was of interest to see what deviation existed between curve A, Fig. 3, and the true intrinsic viscosity vs. methanol concentration curve. The necessary determinations were made with the four dextran dilutions used in obtaining $[\eta]$ at a specific methanol concentration, each containing that concentration of methanol. The curve B, resulting from these determinations, is shown in Fig. 3. As might be expected, curves A and B are somewhat similar.

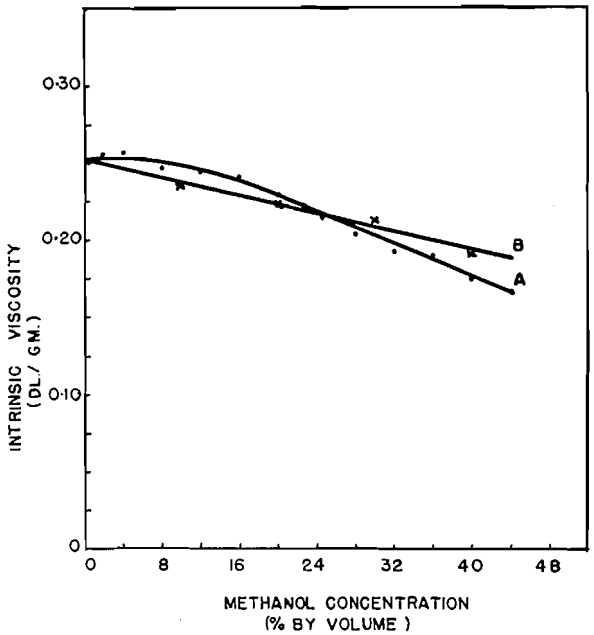

FIG. 3. Intrinsic viscosity of solutions of dextran sample 3 in the presence of 0 to 44% methanol by volume. Curve A—Pseudo intrinsic viscosity vs. methanol concentration. See text. Curve B—True intrinsic viscosity vs. methanol concentration.

Wales and co-workers have shown (7) that the $[\eta]$ of a similar dextran in 40.5% methanol in water was 0.17 as compared with 0.271 in aqueous solution. The results in the present instance are of the same general order. From curve B, which is directly comparable, the figures are, respectively, 0.193 and 0.253. From curve A, which is not directly comparable, the figures are 0.175 and 0.253.

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The common purpose of performing viscosity determinations in the production of dextran plasma expanders is to control the molecular size of the product. The intrinsic or inherent viscosities so measured may be converted to a calculated viscosity average molecular weight for ease of comparison with other materials. If the formula derived by Wales and co-workers (6) for the relation between intrinsic viscosity and weight average molecular weight be used, the unknown presence of 2% of methanol in the test fraction for sample 3 will cause a more than 30% error in the calculated molecular weight. With the use of other formulae (2, 3, 8) the discrepancy will be even greater. The effect of 2% methanol on the light scattering weight average molecular weight is virtually nil. This example serves to emphasize the necessity for exercising great care in viscosity determinations on dextran fractions obtained by methanol precipitation.

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LEAD TETRAACETATE OXIDATION OF OLIGOSACCHARIDES[1]

By A. S. Perlin and A. R. Lansdown[2]

ABSTRACT

Lead tetraacetate oxidation is shown to be useful for examining some structural features of trisaccharides and higher oligosaccharides. Generally, the oxidations follow a course similar to that found with the corresponding disaccharide. In some oligosaccharides, however, glycol groups which resist oxidation are encountered. Such groups are 2,3-*trans* glycols of central residues which are linked to adjacent residues by 1,4-glycosidic bonds. The apparent inability to complex with lead tetraacetate suggests a conformation for these sugar residues in acetic acid solution which differs from that of the corresponding monosaccharide glycopyranoside. Lead tetraacetate oxidation of oligosaccharides in which central residues are unaffected by the reagent constitutes a unique stepwise degradation of these compounds, and possible applications of the reaction are suggested.

An earlier publication (11) described the use of lead tetraacetate oxidation (1, 4) for determining the structure of reducing disaccharides, and suggested that the reaction may also be of value for higher oligosaccharides. Subsequent examination of several oligosaccharides supports this contention.

In some respects the oligosaccharides show oxidation behavior which is closely similar to that of the disaccharides. Thus the yield and rate of production of formic acid from xylotriose and higher oligosaccharides of the same series are almost identical with those from xylobiose (11, Fig. 4). The rapid liberation of one mole of acid appears to result from cleavage of carbon–

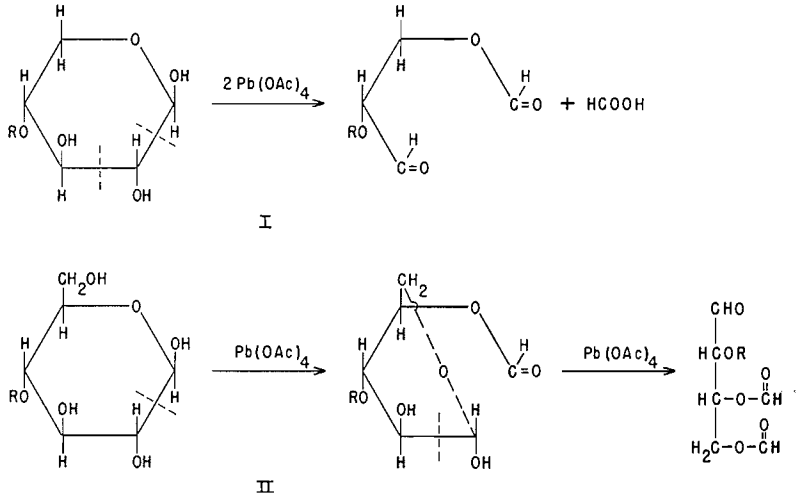

FIG. 1. I. Oxidation of the reducing end-unit of a (1 → 4) xylose oligosaccharide (R = non-reducing residue or residues). II. Oxidation of the reducing end-unit of a (1 → 4) glucose oligosaccharide (R = non-reducing residue or residues).

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carbon bonds 1,2 and 2,3 of the reducing end-unit, carbon-1 being converted to a formate ester (I, Fig. 1) and carbon-2 released as formic acid; the second mole of acid is produced slowly from the non-reducing end. With oligosaccharides of the maltose and cellobiose series the formic acid produced appears to originate almost exclusively from the non-reducing end and, in each instance, at a rate approximately equal to that found for maltose (11, Fig. 1). In these compounds it appears that carbon-2 as well as carbon-1 of the reducing end-unit produces a stable formate ester (II, Fig. 1), and a total yield of only one mole of free acid is obtained.

From the standpoint of formic acid production the oligosaccharides considered above may be regarded as disaccharides since the central residues are glycosidically linked 1,4- and can yield no acid. However, it would be expected that the free 2,3-glycol group of the central residues should cleave oxidatively and lead tetraacetate consumption accordingly increase by one mole for each central unit. That is, xylobiose consumes four moles of oxidant but xylotriose should consume five moles, xylotetraose, six moles, and so on. In fact, however, all three compounds consume approximately four moles of lead tetraacetate per mole during the reaction period examined (Table I). Since this quantity is

TABLE I

LEAD TETRAACETATE OXIDATION OF OLIGOSACCHARIDES*

Compound	Total $Pb(OAc)_4$ consumed†	Formic acid produced	$Pb(OAc)_4$ consumed by compound
Xylobiose	5.8	1.9	3.9
Xylotriose	5.9	2.0	3.9
Xylotetraose	5.3	1.8	3.5
Xylopentaose	5.6	1.9	3.7
Xylohexaose	6.5	2.1	4.4
Maltose	5.2	1.1	4.1
Maltotriose	5.4	1.2	4.2
Maltotetraose	3.9	0.7	3.2
Maltopentaose	5.0	0.9	4.1
Maltohexaose	5.7	0.9	4.8
Cellobiose	4.9	1.1	3.8
Cellotriose	4.5	1.0	3.5
Cellotetraose	5.1	1.1	4.0
Benzyl β-maltoside	3.1	1.0	2.1
Raffinose	6.7	1.9	4.8

**Six-hour reaction period (see Fig. 1).*
†Includes $Pb(OAc)_4$ consumed in oxidation of formic acid to CO_2.

sufficient only to account for the two moles of formic acid produced it appears that the central residues are not attacked by the oxidant. In agreement with this suggestion, after the oxidation of xylotriose one mole of pentose remains intact. Similar results are obtained with compounds of the maltose and cellobiose series (Table I). Approximately four moles of lead tetraacetate are consumed which again corresponds to oxidation only of reducing and non-reducing end-units. In a few instances, the values are only 80–85% of those generally found which is probably due to the fact that these compounds are

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difficult to purify or are highly hygroscopic. Maltohexaose appears to consume an additional mole of oxidant per mole, suggesting that one of the four central residues is attacked.

Benzyl β-D-maltoside also exhibits a similar resistance to oxidation by lead tetraacetate. One mole of formic acid is liberated at a rate close to that of the methyl glucoside, and two moles of oxidant are consumed. These data account only for oxidation of the terminal unit, and one mole of glucose is recovered after hydrolysis of the reaction product.

The resistant sugar residues in these oligosaccharides have one common structural feature—a 2,3-*trans* glycol group subtended by glycosidic linkages at carbons 1 and 4. Lead tetraacetate is known to cleave *trans* glycol groups although less readily than *cis* glycols (4, 7). This has been explained in part by assuming that the cleavage reaction involves formation of a cyclic intermediate (4) which is more easily accommodated by a *cis* than by a *trans* glycol group. Accordingly, the configuration of the 2,3-*trans* glycol of the resistant units of the oligosaccharides may be distorted sufficiently to prevent complex formation. The 2,3-*trans* glycol group of the non-reducing end-unit, however, is readily oxidized and must therefore possess a more favored configuration.

Raffinose affords an oligosaccharide in which the central unit possesses a 2,3-*trans* glycol group but is linked through the 6- rather than the 4-position to an adjacent residue. If the latter linkage position is important for inducing resistance to oxidation, normal attack of the central unit in raffinose would be expected. This, in fact, is found to occur; two moles of formic acid are liberated and a total of five moles of lead tetraacetate consumed (Table I), corresponding to cleavage of all glycol groups in the molecule.

It appears, therefore, that the presence of a glycosidic bond at carbon-4 of a non-reducing sugar unit markedly alters the configuration of the 2- and 3-hydroxyl groups from that normally encountered in the corresponding monomer glycopyranoside. A critical evaluation of glycol-cleavage oxidations by Heidt, Gladding, and Purves (7) led to the assignment of optimal dimensions in glycol groups for complexing with an oxidant. Studies by Reeves on cuprammonium complexes of glycosides likewise suggest conformations which are likely to be less or more prone to glycol-cleavage (12). From these data, the observed resistance of glycol groups in oligosaccharides to oxidation suggests that the sugar units concerned may possess a conformation in acetic acid solution other than Reeves' C-1 form, most commonly encountered with the glycopyranosides of these sugars (12). Steric hindrance to complexing of the glycol group with the oxidant by neighboring sugar residues appears unlikely because differences in the degree of resistance should then have been expected between α- and β-linked compounds, e.g. between maltotriose and cellotriose. It will be of interest to examine other oligosaccharides which have structural features somewhat different from those described above. For example, a trisaccharide in which mannose constitutes a central residue linked 1,4- to the adjacent units would provide a 2,3-*cis* glycol group which would be expected to cleave readily. Considerations of this kind have been recorded

by Dimler (5) in explaining the resistance of ⟨1,4⟩⟨1,6⟩ anhydrohexofuranoses to periodate and lead tetraacetate oxidation. In these hexosans the resistant glycol group is also *trans* but, in contrast to those of the oligosaccharides described, occurs on a furan ring and hence is more likely to have a highly unfavorable bond angle, i.e. about 120° or greater (12).

The current results show that lead tetraacetate oxidation under the conditions described may be of value for determining some structural features of higher oligosaccharides. Limitations are imposed, however, by the resistance to oxidation of some types of glycol groups. For example, distinction between a 1,3- and 1,4-glycosidic linkage in central sugar residues may prove difficult in such instances, requiring collaborative evidence from methylation or periodate oxidation. On the other hand, this behavior can facilitate the determination of the linkage position of the reducing end-unit, as indicated above, or the identification of the central residues of oligosaccharides containing more than one type of monosaccharide residue. The reaction also constitutes a unique means for effecting a partial degradation of many oligosaccharides. Application may therefore be found, for example, in studies with isotopically-labelled compounds. Thus, the specific activity of the central unit in maltotriose could be determined by treating the compound with lead tetraacetate and isolating by hydrolysis the unoxidized glucose. The observed instances of resistance to oxidation, however, question the practice of using lead tetraacetate to test for glycol groups in partially substituted polysaccharide derivatives. Polysaccharides examined, including glycogen and a water-soluble pentosan, did not consume lead tetraacetate during a reaction period of several days' duration. However, these instances of unreactivity may be attributed chiefly to insolubility of the carbohydrates in acetic acid, for otherwise, by analogy with the oligosaccharides, end-groups of the polymers should be oxidized.

EXPERIMENTAL

The oligosaccharides of the cellobiose, maltose, and xylobiose series were kindly furnished, respectively, by Dr. D. R. Whitaker, Dr. R. L. Whistler, and Dr. C. T. Bishop, who have described the compounds elsewhere (15, 14, 2). Benzyl β-maltoside was prepared by the procedure of Lemieux and Lansdown (8). Lead tetraacetate was prepared according to the procedure recommended by Vogel (13), or was obtained commercially from Matheson, Coleman, and Bell, New Jersey.

Oxidation of Oligosaccharides

Reactions were carried out in duplicate at 28°C. in a constant-volume type of Warburg respirometer as described previously (10, 11) using aqueous acetic acid as solvent (1) to facilitate solution of the carbohydrates. In a typical experiment, one milliliter of 90% acetic acid containing 20 mgm. of lead tetraacetate and 10 mgm. of potassium acetate was placed in the vessel, and 1.24 mgm. of xylotriose, dissolved in 0.2 ml. of 90% acetic acid, was placed in the side-arm. After initial equilibration the reaction was initiated by mixing the two solutions and changes in pressure due to evolved carbon

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dioxide were noted at desired intervals, the readings being corrected for pressure changes in the respirometer blank. The rate of evolution of carbon dioxide is represented approximately by curve 2 (11, Fig. 4); in six hours' reaction time the rate had become slow and the yield of carbon dioxide corresponded to a value of 2.0 moles of formic acid per mole of xylotriose. The contents of the vessel were transferred to a glass-stoppered flask by washing with 10 ml. of "stopping" solution (3), and the quantity of lead tetraacetate consumed in the reaction was determined by titration with thiosulphate. The difference in titer between the blank and sample was 7.10 ml. of 0.005 *N* thiosulphate corresponding to 5.9 moles of oxidant consumed per mole of xylotriose. Since 2.0 moles of lead tetraacetate were used in converting the formic acid to carbon dioxide the corrected consumption of oxidant was 3.9 moles per mole (Table I).

In a duplicate experiment, at the end of the six-hour period the reaction mixture was treated with 20 mgm. of oxalic acid, dissolved in 0.2 ml. of glacial acetic acid; this simultaneously reduced excess lead tetraacetate and precipitated the divalent lead. An aliquot of the supernatant solution was then used for colorimetric determination of pentose with the orcinol reagent (9). The quantity of pentose formed using xylobiose, oxidized under the same conditions, as blank corresponded to 0.89 moles of xylose per mole of oxidized xylotriose.

The quantity of glucose remaining after oxidation of benzyl maltoside was determined as follows: after the treatment with excess oxalic acid, as above, the acetic acid was distilled and the residue was dissolved in water and heated at 100°C. for 3.5 hr. The hydrolyzate was then analyzed for glucose by quantitative paper chromatography (6); the glucose content of the solution corresponded to 0.96 mole per mole of benzyl maltoside.

ACKNOWLEDGMENTS

The authors express their appreciation to Dr. C. T. Bishop for his kind interest in this work and, in addition, to Dr. R. L. Whistler and Dr. D. R. Whitaker, for providing oligosaccharide samples.

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THE PAPILIONACEOUS ALKALOIDS

XXII. PUSILLINE; ITS IDENTITY WITH β-ISOSPARTEINE[1]

By R. Greenhalgh[2] and Léo Marion

ABSTRACT

l-Pusilline is shown to be identical with β-isosparteine by direct comparison of the bases and of their salts. By mild oxidation with mercuric acetate followed by catalytic hydrogenation, pusilline is converted to *d*-sparteine, thus confirming its identity with *l*-β-isosparteine. The sparteine obtained from β-isosparteine derived from lupanoline was *d*-sparteine, and not the *l*-form as reported. Oxidation of β-isosparteine with potassium permanganate gives rise to a hydrated 10,17-dioxo-derivative.

l-Pusilline, first isolated from *Lupinus pusillus*, was described as a completely saturated alkaloid yielding analytical figures in agreement with either $C_{15}H_{26}N_2$ or $C_{15}H_{28}N_2$ (3). Since an imino-methyl determination indicated the presence of one such group, the latter empirical formula was adopted (4). Because of the marked similarity between its properties and those of sparteine, pusilline was tentatively represented as 3-(N′-methyl-2′-piperidyl)-quinolizidine. Of the four possible racemates of this structure, one has been synthesized by Winterfeld, Wald, and Rink (9) and two racemates were synthesized by Šorm (8). These, however, were different from the alkaloid.

Reduction of lupanoline, an isomer of hydroxylupanine (5), with lithium aluminum hydride has been shown by Moore and Marion (6) to produce β-isosparteine which was isolated as a diperchlorate. Recently, Carmack, Douglas, Martin, and Suss (1) have established the identity of the alkaloid spartalupine occurring in *L. sericeus* with β-isosparteine and thus recorded the first natural occurrence of the alkaloid. Spartalupine and pusilline both give rise to monoperchlorates which have the same melting point. It has now been shown that pusilline monoperchlorate can be converted to a diperchlorate having the same melting point as β-isosparteine diperchlorate, and having an X-ray powder pattern identical with that of the latter. A comparison of the infrared absorption spectrum of β-isosparteine (see Fig. 3 in Ref. 2) with that of pusilline revealed that each peak appearing in one was present in the other. Furthermore, mild oxidation of *l*-pusilline with mercuric acetate followed by catalytic hydrogenation gave rise to *d*-sparteine identified by comparison of its infrared absorption spectrum with that of an authentic specimen, and also by comparison of its dipicrate with those of both *l*- and *d*-sparteine. This conversion had already been described as occurring with β-isosparteine[3] (6).

A complex picrate had been obtained from pusilline (4). It has now been

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Contribution from the Division of Pure Chemistry, National Research Council, Ottawa, Canada. Issued as N.R.C. No. 3894.
[2]*National Research Council of Canada Post-doctorate Fellow.*
[3]*Through an error, Moore and Marion (6) reported that the β-isosparteine obtained from lupanoline gave rise in this conversion to l-sparteine. This should read d-sparteine. The dipicrate melted at 209° and the melting point was not depressed on admixture with d-sparteine dipicrate; it melted at 203–204° when mixed with l-sparteine dipicrate. It had* $[\alpha]_D$ *+22 (c = 0.09 in methanol). An authentic sample of d-sparteine dipicrate had* $[\alpha]_D$ *+24.5 (c = 0.092 in methanol).*

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shown that pusilline also forms a dipicrate identical with that prepared from β-isosparteine by Dr. Carmack who kindly sent us a specimen. The previously reported analytical determination of an N-methyl group was spurious since repeated determinations with pusilline and pusilline monoperchlorate gave negative results so long as *freshly distilled* hydriodic acid was used.

It has been previously reported by Moore and Marion (6) that the oxidation of β-isosparteine with potassium ferricyanide gives rise to oxo-β-isosparteine ($C_{15}H_{24}ON_2$), which by mercuric acetate oxidation followed by catalytic hydrogenation is converted to 17-oxo-sparteine. If, on the other hand, pusilline was oxidized with potassium permanganate it gave rise to a dioxo-compound which was neutral, and therefore a dilactam. It gave analytical figures in agreement with the formula $C_{15}H_{24}O_3N_2$. Its infrared absorption spectrum showed strong absorption in the region indicative of lactam carbonyls, and also a band in the hydroxyl region. When this compound was distilled *in vacuo* and crystallized from hexane it yielded two forms of crystals which were separated by hand. The first was the hydrate of a dioxo-compound ($C_{15}H_{22}O_2N_2.H_2O$) and the second the anhydrous product. An attempt to hydrogenate the dioxo-hydrate in acid solution over Adams' catalyst at room temperature proved unsuccessful, and this would seem to indicate a 10,17-dioxo structure, particularly in view of the potassium ferricyanide oxidation product.[4]

It can therefore be concluded unequivocally that *l*-pusilline and *l*-β-isosparteine are identical.

EXPERIMENTAL

Pusilline isolated from *L. pusillus* (3) consisted of a colorless oil, b.p. 110–115° at 4 mm., $[\alpha]_D^{32}$ −15.3° (*c*, 2.3 in abs. ethanol). It formed a monoperchlorate, m.p. 216°; a dihydrochloride, m.p. 270–273°; a monohydrochloride hydrate, m.p. 88–90°, resolidified and melted again at 235.5–236.5°; a monohydriodide, m.p. 252.5°; and a complex picrate, m.p. 183.5–185.5° (4).

Conversion of l-Pusilline to d-Sparteine

A small quantity of pusilline in 5% aqueous acetic acid was oxidized with an excess of mercuric acetate according to the usual procedure (6), and the dehydro-base was hydrogenated over Adams' catalyst in acid solution. The base thus obtained was distilled *in vacuo*; its infrared absorption spectrum was superimposable on that of *d*-sparteine. The base formed a dipicrate, m.p. 207–208°, either alone or in admixture with an authentic sample of *d*-sparteine dipicrate. Calc. for $C_{15}H_{26}N_2.2C_6H_3O_7N_3$: C, 46.82; H, 4.66. Found: C, 46.91; H, 4.88%. In admixture with *l*-sparteine dipicrate it melted at 202–203°.

Pusilline Diperchlorate

A quantity of the monoperchlorate of pusilline was dissolved in methanol and the solution neutralized to Congo red with perchloric acid. On standing,

[4]*Dr. Carmack informs us that he has established that the derivative so obtained from β-isosparteine is 10,17-dioxo-β-isosparteine, by comparison with one of the dl-dioxo-intermediates obtained in Sorm and Keil's synthesis (7) of sparteine. A sample kindly supplied by Dr. Carmack did not depress the melting point of our product on admixture.*

the liquor slowly deposited the diperchlorate. It was recrystallized from boiling methanol from which it separated as small, stout, colorless prisms, m.p. 247–249° (dec.), when immersed at 195°. In admixture with authentic *l*-β-isosparteine diperchlorate (6), m.p. 246–248°. The X-ray powder patterns of the two diperchlorates were identical.

Pusilline Dipicrate

Freshly distilled pusilline (15 mgm.) was dissolved in methanol and added to a methanolic solution of picric acid (30 mgm.). The resulting liquor was concentrated on the steam-bath and allowed to cool. It deposited a crystalline picrate which, after recrystallization from methanol, melted at 132–133°. The melting point was not depressed by admixture with a sample of β-isosparteine dipicrate kindly supplied by Dr. M. Carmack.

Oxidation of Pusilline (β-Isosparteine)

A quantity of pusilline in aqueous medium was oxidized with finely powdered permanganate. The addition of permanganate was stopped when the color was retained by the solution for several hours. The precipitated manganese dioxide was filtered, washed with water, and then with chloroform. The filtrate was extracted repeatedly with chloroform and the extract evaporated to dryness. There was left a crystalline product, m.p. 163–165°, which distilled at 90–110° at 0.04 mm. to a hygroscopic, opaque glass. On recrystallizing from hexane this product gave two forms of crystals which were separated by hand. One form consisted of long colorless needles, m.p. 170–171°, which was not depressed in admixture with a sample of dioxo-spartalupine (dioxo-β-isosparteine) hydrate kindly supplied by Dr. M. Carmack. Calc. for $C_{15}H_{22}O_2N_2.H_2O$: C, 64.26; H, 8.63; N, 9.99. Found: C, 64.55; H, 8.52; N, 10.21%. The other forms of crystals consisted of very small clusters, m.p. 154–155°, which gave a large depression when mixed with the substance melting at 170–171°. The analysis of this substance was not too satisfactory. Whereas the hydrogen and oxygen results showed good agreement with the figures required for the anhydrous compound, carbon was somewhat high.

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We wish to acknowledge our indebtedness to Dr. Maria Przybylska for the X-ray powder patterns and to Mr. R. Lauzon for the infrared spectra; also to Dr. Marvin Carmack for his courtesy in giving us samples of β-isosparteine dipicrate and dioxo-β-isosparteine hydrate.

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COMPOSITION OF DELPHINIUM SEED OIL[1]

By Mary J. Chisholm and C. Y. Hopkins

ABSTRACT

The fatty oil of delphinium seed (*Delphinium hybridum* (Hort.)) was examined. Fresh seed gave an oil composed mainly of glycerides but having 2.8% of free fatty acids. The oil from older seed contained about 50% of free fatty acids, apparently as a result of lipase action in the seed. The total fatty acids were found to include *cis*-11-eicosenoic acid (18%) and eicosadienoic acid (1%), the latter identified as tetrahydroxyeicosanoic acid. Other acids that were identified and the estimated percentages were: 9-hexadecenoic <1, palmitic 4, linoleic 16, oleic 53, and stearic 1. Spectroscopic analysis indicated a content of 2.5% of octadecatrienoic acid. Eicosoic acids have not been observed previously in the seed oils of this plant family (Ranunculaceae).

INTRODUCTION

The seeds of various plants of the Ranunculaceae have been observed to contain from 20 to 40% of fatty oil and to have a high lipase activity. Little is known of the composition of the oils. The constants of oils from *Delphinium* species have been recorded by Markwood (9, 10), Ivanov (8), and Hunter (7). One species, *Delphinium staphisagria*, has been studied further by Nath (11) who identified several of the fatty acids of the oil.

In the present work, the fatty acids of *Delphinium hybridum* (Hort.) have been studied in a quantitative manner and some attention has been given to the action of the lipase.

EXPERIMENTAL

Properties of the Oil

The seed examined in the main part of the work (Sample 1) was that of the cultivated delphinium, described as *D. hybridum* (Hort.). It was obtained from a commercial seed house and remained in storage for four years under dry conditions before the oil was extracted. On extraction with petroleum ether the seed yielded 36.1% of oil (basis 10% moisture). Constants of the oil are shown in Table I.

TABLE I

Properties of oil of *D. hybridum* (Hort.), Sample 1

Iodine value	101	Glycerol yield, %	5.0
Saponification value	194	Acetyl value	24.8
Unsaponifiable matter, %	1.0	Acetyl value of methyl esters	6.5
Acid value	100	Peroxide value (iodide method)	3.5
Free acid as oleic, %	50.3		

The high content of free fatty acid, considered to be the result of lipase action in the seed, is accompanied by a low glycerol yield, since glycerol liberated in the seed is known to disappear rapidly. The acetyl value is unusually

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high, probably because of the presence of partially hydrolyzed glycerides. It is reduced considerably when the glycerides are converted to methyl esters.

Seed of another strain of *D. hybridum* (Sample 2) was examined within a few months of harvesting. It yielded 25.7% of oil having iodine value 123 and acetyl value 4.7. This oil gave a glycerol yield of 9.7%. The acid value was 5.5, corresponding to 2.8% of free fatty acid. Evidently lipolysis had progressed to only a slight extent.

Seed of *Delphinium ajacis* (Sample 3) had 39.9% oil of iodine value 95 and acid value 72.1, corresponding to 36.3% of free fatty acid. This seed was more than one year old.

A portion of Sample 1 was saponified and the total fatty acids were freed from unsaponifiable matter. Their ultraviolet absorption, before and after

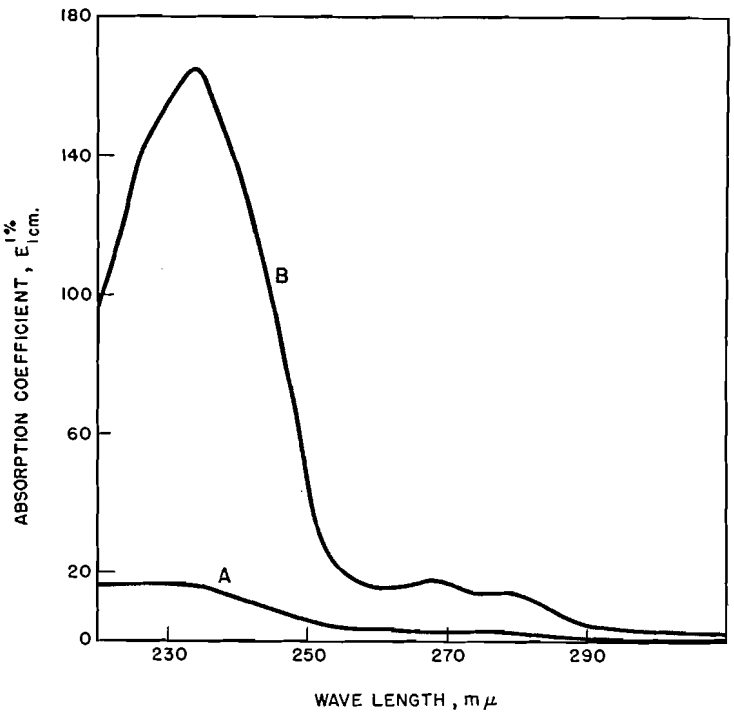

FIG. 1. Ultraviolet spectrum of delphinium fatty acids freed from unsaponifiable matter. *A*, before isomerization; *B*, after isomerization (in glycerol 45 min. at 180°).

alkali isomerization, is shown in Fig. 1. The absorption coefficients ($E^{1\%}_{1\,cm.}$) after isomerization were 164.5 at 233 mμ and 18.1 at 268 mμ, indicating a content of 15.9% of dienoic acid(s) and 2.5% of trienoic acid(s), calculated as octadecoic acids. The calculation is based on absorption coefficients for natural *cis* acids.

Examination of the Methyl Esters

The oil (Sample 1) was converted to methyl esters by methanolysis with acid catalyst (6). The esters (300 gm.) were distilled through a Podbelniak

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Heli-Grid column at a pressure of 0.4 mm., and the residue was transferred to a smaller flask and distilled through a spinning band column. The distillation curve is shown in Fig. 2. It indicates an appreciable content of C_{20} esters. A further lot of esters was hydrogenated and distilled, giving a curve almost identical with the one for the original esters.

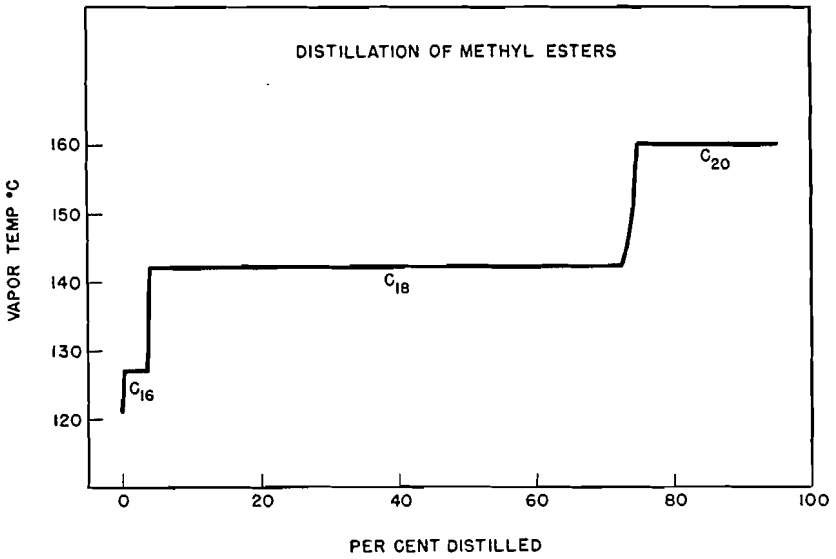

FIG. 2. Distillation of methyl esters.

Distillation data for one lot of the original methyl esters are given in Table II. The distilled fractions were examined individually by the methods

TABLE II

DISTILLATION OF METHYL ESTERS

Fraction	Temp., ° C. (0.4 mm.)	Weight, gm.	Chain length	Iodine value	Refractive index, 25°
1	120–127	1.1		20.3	—
2	127	10.0	C_{16}	6.4	Solid
3	142			116.7	1.4541
4	142	206.0	C_{18}	103.4	1.4528
5	142			95.1	1.4519
6	142–151	4.4		60.9	Solid
7	151–160	1.8		91.4	1.4585
8	160	26.7	C_{20}	81.2	1.4535
9	160	22.9	C_{20}	77.4	1.4529
R	–	17.0			

described previously (3) and the component acids were identified as shown in Table III. Identity of the products was confirmed by mixed melting point except in the case of tetrahydroxyeicosanoic acid, which has not been prepared previously.

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TABLE III

IDENTIFICATION OF ACIDS

Fraction	Acid	Identified as:	Melting point, °C.
1	9-Hexadecenoic	9,10-Dihydroxypalmitic	123.5–124.5
2	Palmitic	Palmitic	62.5– 63
3	Linoleic	Tetrahydroxystearic	172 –173
	Oleic	Dihydroxystearic	129 –130
6	Stearic	Stearic	69 – 70
8	Eicosadienoic	Tetrahydroxyeicosanoic	172 –173
8	11-Eicosenoic	11,12-Dihydroxyeicosanoic	129.5–130.5
9	11-Eicosenoic	11-Eicosenoic N-hydroxyamide	69 – 70

Examination of C_{20} Fractions

Fractions 7 and 8 were found by ultraviolet absorption to contain some diene acid. Fraction 8 was recrystallized from acetone at −45°, giving 22.9 gm. of methyl eicosenoate, iodine value 77.9 (theory 78.2). After saponification and hydroxylation by permanganate, it yielded dihydroxyeicosanoic acid, m.p. 129.5–130.5°. The melting point was not depressed by mixing with authentic 11,12-dihydroxyeicosanoic acid.

The acetone filtrate from the recrystallization of Fraction 8 gave 2.8 gm. of methyl esters of iodine value 102.6, evidently containing the dienoic acid. After saponifying, hydroxylating with permanganate, and boiling the product with ethyl acetate to dissolve dihydroxy acids, the residue was recrystallized from ethanol. It melted at 172–173°. When mixed with tetrahydroxystearic acid of m.p. 172–173°, the melting point was lowered to 162–164°. Accordingly the substance is considered to be tetrahydroxyeicosanoic acid. Calc. for $C_{20}H_{40}O_6$: C, 63.79; H, 10.70. Found: C, 63.99; H, 10.74. Its infrared spectrum is consistent with this structure. The spectrum, determined in Nujol mull, is very similar to but not identical with that of 9,10,12,13-tetrahydroxystearic acid of m.p. 144° (R. N. Jones, to be published).

Fraction 9 was almost pure methyl eicosenoate. Its infrared spectrum showed no peak at 965 cm.$^{-1}$ and accordingly it is judged to be the *cis* form. The molar extinction coefficient ϵ at 965 cm.$^{-1}$ was 12.0 (methyl oleate 12.2).

The C_{20} fraction from the distillation of the hydrogenated esters was pure methyl arachidate, m.p. 45–46°. The small distillation residue was saponified. The acids had equivalent weight 318.9 (arachidic acid, 312.5), indicating that there is a small proportion of acid of greater chain length than C_{20}.

Percentage Composition

Distillation of the hydrogenated esters and examination of the residue gave the following percentages by chain length: C_{16} 5, C_{18} 70, C_{20} 19, C_{22} 1, loss and unidentified residue 5.

Estimation of the fatty acid composition from the entire data, including only those acids actually identified, gives the percentages shown in Table IV (in the order in which the esters distill).

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TABLE IV

ESTIMATED FATTY ACID COMPOSITION (% OF TOTAL FATTY ACIDS)

Acid	%	Acid	%
9-Hexadecenoic	< 1	Stearic	1
Palmitic	4	Eicosadienoic	1
Linoleic	16	11-Eicosenoic	18
Oleic	53	Undetermined	6

The undetermined portion includes about 2.5% of trienes, as indicated by the spectrometric data, mainly in the C_{18} range. There was also some distillation loss and some unidentified material in the residue.

Glyceryl Residue and Lipase Activity

A sample of oil from seed sample 1 was saponified and the fatty acids were removed. The aqueous residue was concentrated and treated with benzoyl chloride. It yielded glycerol tribenzoate, m.p. 71–72° alone and mixed with an authentic sample. Oil from fresh seed was analyzed for glycerol by the method of Colson (4). It gave a glycerol yield of 9.7%.

The free fatty acids were extracted from the oil of Sample 1 and compared with the acids of the remaining glycerides to determine whether the enzyme acts preferentially with respect to type of acid. The free acids were 2 units lower in equivalent weight and 4 units lower in iodine value but it is doubtful whether these differences are sufficient to show any specificity.

There was no appreciable change in acid value during storage of the oil. Evidently the enzyme is destroyed or separated from the oil during the solvent extraction process.

DISCUSSION

The oil examined in this work is unusual in having a considerable content of eicosenoic acid (18%) but only a small amount of acids higher than C_{20}. Two studies of the composition of Ranunculaceae seed oils have been reported by earlier workers. *Nigella sativa* oil was found to contain palmitic, stearic, oleic, and linoleic acids (12). *Delphinium staphisagria* oil was reported by Nath (11) to contain oleic, elaidic, and linoleic acids. Thus there has been no previous record of C_{20} fatty acids in this plant family.

The eicosenoic acid isolated in the present work is the ordinary Δ^{11} isomer. It is now known to occur in appreciable amounts in one or more species of the following plant families: Crucifereae, Buxaceae, Tropaeolaceae, and Ranunculaceae.

The occurrence of eicosadienoic acid, $C_{20}H_{36}O_2$, in animal fats and phospholipids has already been established by several workers. It is considered to be of importance in nutrition. Some evidence of its presence in vegetable fats had been noted when determining unsaturation of C_{20} fractions by iodine values and ultraviolet absorption (1, 5). Until now, however, it does not appear to have been definitely identified as a constituent of a vegetable fat. The amount in the delphinium oil is about 1%.

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D. ajacis seed was shown by Bamann and Ullmann to contain a highly active lipase which was more than twice as effective as *Ricinus* lipase (2). It is considered probable that this enzyme is responsible for the unusually high free fatty acid content found in the oil of *D. ajacis* in the present work. The oils of *D. hybridum* (present work), *D. consolida* (9), and *D. staphisagria* (10) have shown similar high acid values, equivalent to 45% or more of free fatty acids.

It may be pointed out that delphinium seed oil ordinarily contains a small percentage of alkaloids.

ACKNOWLEDGMENTS

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DECOMPOSITION OF SODIUM HYPOCHLORITE: THE UNCATALYZED REACTION[1]

By M. W. Lister

ABSTRACT

The decomposition of sodium hypochlorite has been re-examined. The results show that Foerster and Dolch's mechanism of the decomposition to chlorate and chloride is correct; they postulated a slow bimolecular reaction to chlorite and chloride, followed by a faster reaction of chlorite with more hypochlorite. Values of the rate constants of both steps are reported; they make the activation energies 24.8 kcal./gm-molecule for the first step and 20.8 kcal./gm-molecule for the second. The rates are such that at 40° C. a solution of sodium hypochlorite will contain about 1% as much chlorite as hypochlorite. The rate is strongly affected by changing ionic strength; at low ionic strengths it is nearly constant or falls slightly; above about 0.8, the rate rises and at high ionic strengths the rise is quite rapid. No signs of specific catalytic effects of sodium chloride, hydroxide, or carbonate could be observed, and it seems probable that earlier reports of this were due to variations in ionic strength. The decomposition to chloride and oxygen has been measured and is a unimolecular reaction, which is possibly, but not certainly, uncatalyzed. Values of its rate constant are reported; they also are much altered by changing the ionic strength.

Although this reaction was first investigated a considerable number of years ago, there are several matters connected with it that are still not entirely clear. Briefly, the position seems to be this. The best early work on the subject was that of Foerster and his co-workers, particularly Foerster and Dolch (2). They found it to be a second order reaction, and consequently deduced that the mechanism was:

$$2NaOCl \rightarrow NaClO_2 + NaCl$$
$$NaOCl + NaClO_2 \rightarrow NaClO_3 + NaCl\,.$$

The first step is the slower. They showed by an independent experiment that the second step was indeed faster, and their rate constants gave activation energies of $22\frac{1}{2}$ and $20\frac{1}{2}$ kcal./gm-molecule for the first and second step respectively. In addition to the reactions given above it has long been known that decomposition to sodium chloride and oxygen also occurs. Foerster and Dolch's rates are the total reaction rates, though they knew that the reaction to chlorate was very much the more important. They also found that the rate increased as they added sodium hydroxide. Later Giordani (3) investigated the reaction, and concluded that it was a combination of a termolecular reaction giving chlorate, and a bimolecular reaction giving oxygen. He also found a marked effect of sodium hydroxide, but in the opposite direction from that found by Foerster; and, at least from about 0.5 to 1.0 *M* sodium hydroxide, obtained rate constants proportional to $(NaOH)^{-2}$. He therefore assumed that hypochlorous acid was essential to the reaction, and that it went in one step, as follows:

$$OCl^- + 2HOCl \rightarrow ClO_3^- + 2HCl\,.$$

He proposed that the reaction to oxygen was

$$2OCl^- \rightarrow 2Cl^- + O_2\,.$$

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Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario.

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Skrabal and Skrabal (6) examined the dependence of rate on pH, and agreed with Foerster (and Giordani) that the rate was second order at high pH. Pierron (5) examined the relative stability of lithium, sodium, and potassium hypochlorites. He seemed to favor Giordani's mechanism, but supposed that alkali metal peroxides were formed in the alkaline solutions, and that these promoted the reaction. Barredo (1) examined the reaction and found it to be second order; but he also found the rate to be altered by addition of chloride, and over a certain range the rate was proportional to the chloride concentration. He believed that this explained Giordani's results. Such a dependence on chloride concentration would of course make the reaction autocatalytic. The present author (4) has examined the rate of decomposition of neutral or slightly acid hypochlorite solutions, and found that under these conditions the main decomposition was of hypochlorous acid molecules, by a second order reaction. It can be calculated from these results (combined with those in the present paper) that once quite a small excess of sodium hydroxide is present, the concentration of hypochlorous acid is so slow as to make only a negligible contribution to the total decomposition.

It seemed possible that these reported effects of sodium hydroxide and chloride might really be due to changes in the ionic strength. In earlier work the ionic strength was not always kept constant from run to run; and it is not always possible in re-examining the data to deduce what the ionic strength really was. Accordingly the effect of ionic strength on the rate of reaction was examined in the present work. Foerster and Dolch's results seemed to establish that the reaction was second order; however, in view of contradictory later results, this point was checked.

Sodium hypochlorite decomposes both to chlorate and chloride, and to oxygen and chloride. The relation between these reactions was by no means clear, and the oxygen evolution had been relatively little investigated. Hence in the present work the two reactions were measured, so that their kinetics could be determined separately. Since the reaction to oxygen is strongly catalyzed by certain metallic oxides, notably copper or nickel oxides, there has always been some doubt that there really is any appreciable uncatalyzed evolution of oxygen. Hence in the present work, an attempt was made to be sure that the oxygen evolution was not catalyzed; and to find the order of this reaction, and the effect on the rate of varying temperatures or ionic strength.

MATERIALS AND EXPERIMENTAL METHODS

Sodium Hypochlorite

This was produced in solution by the usual method of passing chlorine through cold sodium hydroxide solution. The product always contained a small excess of sodium hydroxide to avoid hydrolysis to hypochlorous acid. The chief uncertainty with these solutions was that they might contain traces of metallic oxide which could act as a catalyst. Such impurities could easily be present in any commercial sample of sodium hydroxide to an extent that would be undesirable, and it would be very difficult to measure how much

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was present accurately enough to allow for its catalytic effect. It was found however that if nickel or copper salts were added to the hypochlorite solution, they could be removed by the following procedure. A small amount of calcium chloride was added, and then enough aqueous sodium carbonate to precipitate all the calcium. The calcium carbonate was filtered off by a sintered glass disk. It was found that if this procedure was repeated four or five times, the rate of gas evolution fell rapidly to a constant low value; further precipitations did not reduce the rate any more. Presumably this procedure removed the copper or nickel salts by coprecipitation with the calcium carbonate. The fact that a final slow rate was reached is some evidence that this was the rate of the uncatalyzed reaction. It was checked that calcium carbonate did not affect the rate; nor did pyrex glass, since the same rate was obtained in a polyethylene flask.

Sodium Chlorite

This was the best available commercial material, manufactured by the Mathieson Alkali Works, recrystallized from water. It contained about 0.04% of chlorate, and a trace of chloride.

Sodium Carbonate

The reagent grade of sodium carbonate, manufactured by Merck Chemical Co., was recrystallized from water.

Sodium Chloride

The reagent grade of sodium chloride, manufactured by the General Chemical Co., was recrystallized from water.

Apparatus

The solutions were contained in a 1-liter flask fitted with (i) a mercury sealed stirrer, (ii) a side arm, normally closed, through which samples could be taken, and (iii) a glass capillary tube leading to a water-jacketed gas burette. The flask was immersed in a water thermostat of conventional design, which was found to maintain the temperature over long periods of time to $\pm 0.1°$ C., though the swing during any on–off cycle was only about 0.02° C. The temperature was read on a thermometer graduated to 0.1° C.

The oxygen evolved was measured in a gas burette graduated in 0.1 ml. In practice the volume could be easily read to 0.05 ml. In reducing the observed volumes to N.T.P. it was always assumed that the oxygen was saturated with water vapor at the temperature of the burette. The confining liquid was mercury, but during a run a trace of water usually condensed out of the oxygen, especially in the runs at higher temperature. The pressure of the oxygen was adjusted to atmospheric pressure, as shown by a small mineral oil manometer; the atmospheric pressure was noted to the nearest $\frac{1}{2}$ mm.

Analytical Methods

The solutions were analyzed at various times for sodium chloride, hypochlorite, chlorite, chlorate, hydroxide, and carbonate. The methods were the same as those outlined by the author in a previous paper (4).

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EXPERIMENTAL PROCEDURE

The general procedure in almost all runs was as follows. A quantity of the stock hypochlorite solution was poured into the reaction flask, the amount added being weighed to the nearest 0.1 gm. Sodium chloride, sodium carbonate, or water (as required) were also weighed out and added. The final volume was always close to 900 ml. When appreciable additions were made to the stock hypochlorite solution, a sample was pipetted out and its density determined; from this the volume of solution could be found, so that the oxygen evolution per liter of solution could be calculated.

The flask was then brought to the right temperature in the thermostat, and at intervals samples were taken for analysis. Between samples the gas evolution was followed by means of the gas burette. It was found that the gas evolution was usually slower at first but built up to a practically constant rate. It is believed that this is due to the building up of a certain degree of supersaturation in the solution, and that eventually the steady rate of gas evolution equals the true reaction rate; it is always the steady rate that is reported in the following data.

The only exceptions to this procedure were in two runs intended to discover whether the pyrex flask catalyzed the reaction. In one of these the flask was filled with pyrex beads, and in the other a polyethylene flask was used. These runs are not reported in detail, but it was found that they gave the same rates as in the ordinary pyrex flask. It was also checked that calcium carbonate, which might be present in traces from the purification process, did not affect the rate. In a few runs sodium chlorite solutions were used, but the general procedure was the same.

EXPERIMENTAL RESULTS

The results for the decomposition of the stock hypochlorite solution at various temperatures are given in Table I. Table II gives various rates of gas evolution. In this table are given data on some runs which were done with filtered hypochlorite solution, but which had not had the complete calcium carbonate treatment. These gas rates are high relative to later runs, so their rate constants for oxygen evolution have little significance; however the data are needed for calculations on the rates of reaction leading to chlorate. It is believed that the rate constants of the reaction to chlorate obtained from these runs are reliable, since (i) it was found that the purification process did not affect the rate of chlorate production, but only that of oxygen, and (ii) it was found (to anticipate results which will be reported later) that catalysts such as copper oxide did not affect the rate of chlorate formation. These runs are also of interest because they show that the rate of gas formation is proportional to the hypochlorite concentration, at least in these solutions; and they throw some light on the activation energy of the (presumably) uncatalyzed reaction to oxygen. Table III shows the effect of ionic strength on the rate constant to chlorate, and Table IV shows the effect of ionic strength on oxygen evolution. Table V gives results on the effect of sodium carbonate, and sodium hydroxide. Table VI gives data on the chlorite–hypochlorite reaction.

TABLE I

Run	Temp., ° C.	Time, min.	(ClO^-), *M*	(ClO_2^-), *M*	(ClO_3^-), *M*	(NaCl), *M*	Remarks
1	40	0	1.556	0.007	0.044	1.80	Ionic strength 3.79
		138	1.548	0.008	—		
		289	1.545	0.0075	0.047		(NaOH) = 0.32 *M*
		581	1.532	0.008	0.051		(Na_2CO_3) = 0.02 *M*
		1244	1.506	0.0075	0.059	1.83	
2	50	0	1.497	0.0095	0.061	1.84	As in run 1
		171	1.476	0.010	0.067		
		279	1.457	0.013	0.070		
		521	1.433	0.012	0.079	1.89	
3	60	0	1.356	0.011	0.105	1.94	As in run 1
		112	1.316	0.015	0.112		
		250	1.278	0.010	0.128		
		380	1.237	0.011	0.138	2.02	
4	40	0	1.201	0.006	0.152	2.05	As in run 1
		193	1.192	0.008	0.154		
		409	1.187	0.009	0.154		
		1386	1.164	0.007	0.162	2.08	
5	60	0	1.134	0.007	0.174	2.09	As in run 1
		353	1.045	0.009	0.199		
		660	0.991	0.0075	0.219		
		1318	0.883	0.006	0.250		
		1754	0.822	0.006	0.268	2.31	
6	50	0	1.481	0.009	0.178	1.84	As in run 1
		347	1.434	0.007	0.088		
		658	1.397	0.010	0.103	1.90	
7	50	0	1.320	—	—	1.96	As in run 1
		356½	1.283				
		659	1.253				
		1441	1.185				
		2124	1.129				
		3061	1.055				
		4434	0.973				
		4975	0.943				
		5874	0.898				
		6370	0.869	—	—	2.28	
8	60	0	0.973	0.007	0.015	2.48	Ionic strength 3.63
		82	0.961				
		210	0.942				(NaOH) = 0.042 *M*
		302	0.929				(Na_2CO_3) = 0.036 *M*
		443½	0.908				
		590	0.889				
		1252	0.808				
		1450	0.785	—	—	2.61	

TABLE II

Run	Temp., ° C.	Mean (ClO^-), gm-mol./l.	Gas rate, ml. N.T.P./min. per l. of soln.	K_0, $min.^{-1}$
1	40	1.545	0.0405	2.34×10^{-6}
		1.525	0.0375	2.20
		1.505	0.039	2.31
4	40	1.19	0.0325	2.44
		1.16	0.0315	2.42
2	50	1.48	0.114	6.88
		1.43	0.108	6.74
7	50	1.17	0.091	6.94
		0.885	0.067	6.99
3	60	1.325	0.288	19.25
		1.295	0.279	19.2
		1.26	0.282	19.95
5	60	1.035	0.225	19.4
		0.855	0.187	19.5

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TABLE III

Run	Temp., ° C.	Ionic strength	Time, min.	(ClO^-), *M*	(ClO_2^-), *M*	(ClO_3^-), *M*	(NaCl), *M*	Remarks
9	60	5.83	0	0.987	0.010	0.192	4.20	(NaOH) = 0.32 *M*
			143	0.947	0.008			($NaCO_3$) = 0.02 *M*
			223½	0.927				
			427½	0.882				
			506½	0.861	0.004	0.235	4.37	
10	60	4.84	0	1.182	0.014	0.145	3.14	As in run 9
			124½	1.135				
			297	1.083				
			411	1.046	0.015	0.185	3.23	
14	60	4.71	0	1.137	0.009	0.144	3.07	(NaOH) = 0.28 *M*
			410	1.021				(Na_2CO_3) = 0.02 *M*
			1367	0.816	0.010	0.243	3.28	
19	60	4.16	0	1.719	0.022	0.029	1.95	(NaOH) = 0.29 *M*
			62	1.684	0.020	0.039		(Na_2CO_3) = 0.05 *M*
			126	1.650	0.016	0.053		
			383	1.506	0.017	0.094	2.08	
11	60	3.79	0	1.164	0.010	0.165	2.07	(NaOH) = 0.32 *M*
			394	1.077	0.010	0.191		(Na_2CO_3) = 0.02 *M*
15	60	3.69	0	0.862	0.010	0.240	2.23	(NaOH) = 0.29 *M*
			458	0.805				(Na_2CO_3) = 0.02 *M*
16	60	2.76	0	0.865	0.007	0.101	1.50	(NaOH) = 0.18 *M*
			346	0.834				(Na_2CO_3) = 0.03 *M*
			949	0.784				
			1332	0.759	0.007	0.134	1.57	
12	60	2.73	0	0.864	0.007	0.111	1.48	(NaOH) = 0.23 *M*
			144	0.854				(Na_2CO_3) = 0.01 *M*
			285	0.843				
			493	0.821				
			627	0.809	0.006	0.129	1.50	
20	60	2.61	0	0.923	0.014	0.038	1.28	(NaOH) = 0.28 *M*
			146	0.915				(Na_2CO_3) = 0.03 *M*
			349	0.895				
			1139	0.812				
			1749	0.757				
			2561	0.695	0.008	0.107	1.43	
17	60	1.74	0	0.539	0.004	0.064	0.88	(NaOH) = 0.19 *M*
			778	0.519				(Na_2CO_3) = 0.02 *M*
			2321	0.483	0.006	0.079	0.92	
21	60	1.75	0	0.710	0.006	0.028	0.88	(NaOH) = 0.06 *M*
			389	0.695				(Na_2CO_3) = 0.02 *M*
			1246	0.658				
			1828	0.638				
18	60	0.59	0	0.1625	0.002	0.0185	0.26	(NaOH) = 0.11 *M*
			733	0.161				(Na_2CO_3) = 0.01 *M*
			2296	0.158	0.003	0.019		
13	60	0.515	0	0.1630	0.002	0.023	0.27	(NaOH) = 0.05 *M*
			235	0.1616				(Na_2CO_3) = 0.00 *M*
			700	0.1553				
			1295	0.1518				
			2012	0.1494	0.001	0.026	0.29	
24	50	2.61	0	1.008	0.007	0.022	1.22	(NaOH) = 0.28 *M*
			269	0.997				(Na_2CO_3) = 0.03 *M*
			464	0.990				
			1202	0.960	0.008	0.033	1.25	

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TABLE IV

DATA ON RATES OF EVOLUTION OF OXYGEN

Run	Temp., °C.	Ionic strength	Mean (ClO^-), gm-mol./l.	Gas rate, ml. N.T.P./min. per l. of soln.
9	60	5.83	0.965	0.276
			0.935	0.243
			0.87	0.241
10	60	4.84	1.16	0.247
			1.065	0.231
14	60	4.71	1.105	0.216
			1.01	0.199
15	60	3.69	0.845	0.0885
16	60	2.76	0.84	0.052
			0.77	0.050
17	60	1.74	0.52	0.028
			0.48	0.024
18	60	0.59	0.16	0.009
21	60	1.75	0.70	0.033
			0.65	0.030
22	70	1.75	0.60	0.062
23	75	1.75	0.56	0.099

TABLE V

EFFECT OF SODIUM HYDROXIDE AND CARBONATE

Run	Temp., °C.	Time, min.	(ClO^-), *M*	(ClO_2^-), *M*	(ClO_3^-), *M*	Remarks
25	50	0	1.127	0.009	0.070	Ionic strength 4.57
		307	1.102			(NaOH) = 0.28 *M*
		987	1.047			(Na_2CO_3) = 0.51 *M*
		1217	1.032	0.009	0.099	
26	50	0	1.377	0.012	0.086	Ionic strength 4.25
		380	1.337			(NaOH) = 0.07 *M*
		1356	1.233	0.011	0.133	(Na_2CO_3) = 0.265 *M*
27	60	0	1.262	0.011	0.118	Ionic strength 3.70
		186½	1.218			(NaOH) = 0.023 *M*
		292	1.189			(Na_2CO_3) = 0.019 *M*
		381	1.166	0.010	0.150	
28	50	0	1.135	0.009	0.161	Ionic strength 3.73
		222	1.119			(NaOH) = 0.275 *M*
		545	1.090			(Na_2CO_3) = 0.04 *M*
		1319	1.041			
		1686	1.014	0.009	0.192	
22	70	0	0.620	0.0065		Ionic strength 1.75
		269	0.5925			(NaOH) = 0.06 *M*
						(Na_2CO_3) = 0.02 *M*
23	75	0	0.5665			As in run 22
		147	0.550			

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TABLE VI

DATA ON CHLORITE–HYPOCHLORITE REACTION
Ionic strength 3.79

Run	Temp., °C.	Time, min.	(ClO^-), *M*	(ClO_2^-), *M*	(ClO_3^-), *M*
29	40	0	0	0.762	0.002
		1784	0	0.762	0.003
30	60	0	0	0.754	0.003
		1287	0	0.755	0.003
31	50	0	1.301	0.180	0.122
		52	1.275	0.148	
		89	1.248	0.133	
		135	1.230	0.111	
		226	1.201	0.081	0.220
32	50	0	0.972	0.345	0.267
		37	0.937	0.311	
		84	0.899	0.278	
		128	0.869	0.249	
		171	0.844	0.225	
		302	0.781	0.168	
		398	0.751	0.139	
33	45	0	1.239	0.284	0.115
		65	1.202	0.248	
		148	1.165	0.210	
		224	1.133	0.184	
		318	1.096	0.146	
34	40	0	1.230	0.324	0.105
		49	1.213	0.306	
		83	1.195	0.295	
		151	1.175	0.273	
		203	1.160	0.257	
		270	1.138	0.242	
		335	1.119	0.226	
		567	1.072	0.176	
		669	1.052	0.161	

DISCUSSION OF RESULTS

It is apparent from these results that the main reaction in the decomposition of sodium hypochlorite is the one to chlorate, and only a small part goes to oxygen. Consequently the over-all kinetics are those of the reaction to chlorate, and the results of Table I fit the equation of a second order reaction: this can be seen from the long run, run 7, or by comparing runs 1 and 4, or 3 and 5. The possibility of catalysis by chloride, or effects of sodium hydroxide, will be considered later when the rate constants have been evaluated. Table II shows that for these runs the reaction to oxygen is first order, though owing to the relatively small amounts of gas evolved the rates are not very accurate. Any comparisons of this sort must be made between runs at the same ionic strength; fortunately the decomposition of hypochlorite does not change the ionic strength during a run.

The mechanism of the reaction is evidently that proposed by Foerster, with

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the addition of the reaction to oxygen. Let the rate constants of the various reactions be k_1, k_2, and k_0 as follows:

$$\begin{aligned} 2NaOCl &\rightarrow NaCl + NaClO_2 && k_1 \\ NaOCl + NaClO_2 &\rightarrow NaCl + NaClO_3 && k_2 \\ NaOCl &\rightarrow NaCl + \tfrac{1}{2}O_2 && k_0 \end{aligned}$$

and let the concentrations be: $(ClO^-) = x$, and $(ClO_2^-) = y$. Then the rate equations are (assuming no effect of chloride):

[i] $$dx/dt = -k_1x^2 - k_2xy - k_0x$$

[ii] $$dy/dt = \tfrac{1}{2}k_1x^2 - k_2xy.$$

These equations are difficult to solve rigorously, but various simplifying assumptions can be made appropriate to the conditions of the reaction. In particular the chlorite concentration is low and changes very little during a run; so approximately $dy/dt = 0$. Equation [i] then becomes:

$$dx/dt = -\tfrac{3}{2}k_1x^2 - k_0x$$

whose solution is most useful in the form:

[iii] $$\frac{1}{x} = \frac{1}{x_0} + \frac{b}{k_0}(e^{k_0 t} - 1)$$

where $x = x_0$ at $t = 0$; and $b = \tfrac{3}{2}k_1 + k_0/x_0$.

To evaluate k_1 it seemed simplest to plot $1/x$ against t, and to determine the slope of the best line through the points. Calling this slope s, we get:

$$s = \frac{1/x - 1/x_0}{t} = \frac{b}{k_0 t}(e^{k_0 t} - 1) = b(1 + \tfrac{1}{2}k_0 t + \tfrac{1}{6}k_0^2 t^2 + \ldots).$$

As $k_0 t$ is always small (never above 0.04), to a good approximation:

$$s = b(1 + \tfrac{1}{2}k_0 t)$$

and

[iv] $$\tfrac{3}{2}k_1 + k_0/x_0 = s(1 + \tfrac{1}{2}k_0 t)^{-1}.$$

k_0 was determined as explained in the next paragraph, and k_1 was then found from equation [iv]. It will be seen that k_1 could also be obtained from the chlorate concentrations, and this was occasionally done, but the hypochlorite analyses are probably the more accurate.

For the determination of k_0, let v be the quantity of oxygen evolved at time t, in units of gm-atoms of oxygen per liter of solution. Then:

$$dv/dt = k_0x.$$

Putting in the value of x from equation [iii], integrating, and since $v = 0$ at $t = 0$, we get:

[v] $$v = \frac{2k_0}{3k_1} \cdot \ln\left[\frac{3k_1x_0}{2k_0}(1 - e^{-k_0 t}) + 1\right].$$

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This is awkward to apply, but suppose we take as an approximate value of k_0:

$$[vi] \qquad k_0(\text{approx.}) = \frac{v/t}{\frac{1}{2}(x+x_0)},$$

i.e. the average rate of gas evolution divided by the mean hypochlorite concentration during the measuring period; then from equations [iii] and [v], expanding in powers of t up to t^2:

$$k_0(\text{approx.}) = k_0[1+\tfrac{1}{4}(k_1x_0+\tfrac{2}{3}k_0)(3k_1x_0-k_0/2)t^2] .$$

The term in t^2 gives the error introduced by this approximation for k_0. Using typical figures for 60° C., this term is about $2.5\times10^{-8}t^2$. The gas collection period never ran above 400 min., when the error is about 0.4%. Hence this approximation is sufficiently accurate. The values of k_1 and k_0 given below are from equations [iv] and [vi]. The evaluation of k_2 will be discussed in a later section.

The results in Table II give values of k_0 which are appreciably higher than those obtained for the most carefully purified solutions. Nevertheless these results are of interest as showing that the gas rate is proportional to the hypochlorite concentration (at least for these solutions); and the data are needed in evaluations of k_1. The mean k_0 values for each run are:

Run	1	4	7	2	3	5	
Temp.	40	40	50	50	60	60	° C.
k_0	2.28	2.48	6.95	6.81	19.45	19.4	$\times10^{-6}$ min.$^{-1}$

The average k_0 at each temperature was used in obtaining k_1 for these runs. It is interesting to note that although a trace of impurity must be present, these runs give an apparent activation energy of about 21 kcal./gm-mol., which is considerably higher than for any of the catalyzed reactions that were examined.

The effect of ionic strength can be obtained from Tables III and IV. From the gas rates in Table IV, we get:

Run	9	10	14	15	16	21	17	18	
Ionic strength	5.83	4.84	4.71	3.69	2.76	1.75	1.74	0.59	
k_0 (60° C.)	25.1	19.2	17.6	9.4	5.7	4.2	4.7	5.0	$\times10^{-5}$ min.$^{-1}$

k_0 varies considerably with ionic strength. As will be seen in the next section, a parallel change is also found for k_1. The results in runs 21, 22, and 23 enable k_0 to be found at different temperatures but the same ionic strength. The results are:

Temp.	60	70	75	° C.
k_0	4.2	9.2	16	$\times10^{-6}$ min.$^{-1}$

These make the activation energy about 20 kcal./gm-mol. Rather surprisingly this is lower than from runs 1 to 7, but possibly the difference is due to experimental error, for the actual rates are very small. However the value seems to be about 20 to 21 kcal. It is also surprising that the activation energy seems to be lower than for the reaction to chlorate. This makes it doubtful that we have an uncatalyzed reaction; the catalyst is not pyrex glass, nor cobalt,

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nickel, or copper (which give lower activation energies). However it is impossible to be sure that traces of some unknown catalyst are not present, and there must remain this element of doubt in the interpretation of the results.

The runs in Table I give the k_1 values in Table VII. It will be seen, for instance by comparison of the rate constants of runs 3, 5, and 11, that the

TABLE VII

Run	Temp., ° C.	k_1, min.$^{-1}$(gm-mol./l.)$^{-1}$	(NaCl), *M*		Ionic strength
			Initial	Final	
1	40	1.04 $\times 10^{-5}$	1.80	1.83	3.79
4	40	1.00	2.05	2.08	3.79
2	50	3.54	1.84	1.89	3.79
6	50	3.68	1.84	1.90	3.79
7	50	3.62	1.96	2.28	3.79
3	60	11.46	1.94	2.02	3.79
5	60	11.32	2.09	2.31	3.79
8	60	10.48	2.48	2.61	3.63

purification did not affect k_1; to anticipate results reported in another paper, addition of catalysts such as copper also did not affect k_1. Table VII also gives the sodium chloride concentrations during the runs. All these runs except run 8 were at an ionic strength of 3.79; in run 8 it was 3.63. Hence it is possible to discover whether sodium chloride has a specific catalytic effect, apart from its contribution to the ionic strength. Although the range of concentrations might perhaps have been profitably extended, these runs definitely show that sodium chloride has no effect on k_1, provided the ionic strength remains unchanged. In particular, run 8 gives a value of k_1 perhaps slightly low for this ionic strength, although the sodium chloride concentration is some 25% higher than in run 3. The long runs 5 and 7 show no sign of autocatalysis, although the sodium chloride increased 10–15% during them. Further evidence in support of this contention is provided by the runs with sodium carbonate present. At an ionic strength of 3.79 the mean rate constants are:

Temp.	40	50	60	° C.
k_1	1.02	3.61	11.4	$\times 10^{-5}$ min.$^{-1}$(gm-mol./l.)$^{-1}$

These give a good linear plot of log k_1 against $1/T$, and make the activation energy 24.8 (to the nearest 0.2) kcal./gm-mol. Foerster's constants at 25° and 90° C. give a value close to 26 kcal., but his result at 50° C. does not fall on a straight line with these values in a plot of log k_1 against $1/T$.

Turning now to the effect of ionic strength on k_1, we get from Table III for k_1 at 60° C.:

Run	9	10	14	19	11	15	8	16	12
Ionic strength	5.83	4.84	4.71	4.16	3.79	3.69	3.63	2.76	2.73
k_1	17.4	16.75	15.65	12.1	11.4	11.2	10.5	7.7	7.8

Run	20	17	21	18	13	
Ionic strength	2.61	1.74	1.75	0.59	0.515	
k_1	7.6	5.5	5.4	3.85	4.3	$\times 10^{-5}$ min.$^{-1}$(gm-mol./l.)$^{-1}$

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These values give somewhat the same type of trend that might be expected for the activity coefficients of sodium hypochlorite over this range of ionic strengths. The trend in k_0 is somewhat, though not very, similar.

Run 24 makes $k_1 = 1.98 \times 10^{-5}$ min.$^{-1}$(gm-mol./l.)$^{-1}$ at 50° C. and an ionic strength of 2.61. This is proportionally a somewhat larger drop than at 60° C., but not very much. Runs 25 and 26 (Table V) give the effect of adding sodium carbonate; they make k_1 at 50° C.:

Run	25	26	
Ionic strength	4.57	4.25	
k_1	4.25	3.95	$\times 10^{-5}$ min.$^{-1}$(gm-mol./l.)$^{-1}$
(NaCl) initial	1.58	1.99	M

Relative to the more carefully measured rate at an ionic strength of 3.79 these runs show an increase in k_1 which is nearly what might be expected purely from the increase in ionic strength. The increase is perhaps a little less than in the runs when sodium chloride was added: of course specific effects are bound to occur, and one would not expect two different salts to give exactly the same change in k_1 for the same change in ionic strength. This is especially so when the two salts, as here, are not of the same ionic type. Nevertheless the main changes in k_1 do seem to be attributable to the changes in ionic strength.

Runs 21, 22, and 23 enable us to evaluate k_1 at three temperatures at another ionic strength (1.75):

Run	21	22	23	
Temp.	60	70	75	° C.
k_1	5.4	16.0	24.0	$\times 10^{-5}$ min.$^{-1}$(gm-mol./l.)$^{-1}$

The figures at the higher temperatures are rather rough; they give a moderately linear plot of log k_1 against $1/T$, with a slope corresponding to an activation energy of about 24 kcal. The experimental error is too large to say whether there is any real difference between the activation energies at ionic strengths of 3.79 and 1.75.

Table V gives the data at low sodium hydroxide concentrations. The bulk of the runs in this paper were done in the presence of 0.32 M sodium hydroxide. Some of the runs at low sodium hydroxide concentrations have already been considered, and found to fall into line with the other runs (e.g. runs 8 and 21). The k_1 values for various runs which provide evidence on the effect of sodium hydroxide are as follows:

Run	(mean)	27	8	21	17	(mean)	28	
Temp.	60	60	60	60	60	50	50	° C.
Ionic strength	3.79	3.70	3.63	1.75	1.74	3.79	3.73	
(NaOH)	0.32	0.023	0.042	0.057	0.19	0.32	0.275	M
k_1	11.4	10.9	10.5	5.42	5.48	3.60	3.48	

These results show that sodium hydroxide has a negligible effect apart from its contribution to the ionic strength. At very low sodium hydroxide concentrations hydrolysis to hypochlorous acid and its decomposition become important; but the rate of this reaction has been measured (4), and it can be calculated that the sodium hydroxide would have to be close to 0.001 M before this reaction made much difference to the total rate.

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Finally the results in Table VI give information on the hypochlorite–chlorite reaction. Firstly runs 29 and 30 show that the decomposition of chlorite by itself is entirely negligible. From the remaining runs k_2 was evaluated as follows. As one molecule of chlorite removes one of hypochlorite, and since this reaction is much faster than the decomposition of hypochlorite (k_1), then approximately:

$$dx/dt = dy/dt = -k_2xy$$

where, as before, x is hypochlorite and y is chlorite. The solution of this equation is:

[vii] $$\frac{\ln (x-c)x_0}{xy_0} = \frac{\ln\ yx_0}{y_0(y+c)} = -ck_2t$$

where $c = x_0-y_0$. In reactions of this sort k_2 is normally obtained from this equation, but in the present case a small correction has to be applied for the decomposition of the hypochlorite, which is slow but not negligible in comparison. It therefore seemed simpler to take an approximate value of k_2 defined by

$$k_2(\text{approx.}) = \text{corrected rate}/(\text{mean } x)(\text{mean } y)\ .$$

By "corrected rate" is meant dx/dt between any two successive readings minus the part of the rate due to decomposition of hypochlorite, which can be calculated from k_1. If the values of x and y from equation [vii] are substituted in this expression, and the exponentials expanded in powers of t, we get:

[viii] $$k_2(\text{approx.}) = k_2[1-(x_0^2+x_0y_0+y_0^2)(k_2^2t^2/12)+\ \ldots\ ]\ .$$

This gives the error in k_2 in this approximation: in the runs reported it rose to about 1%, but the error could then be allowed for. To examine the validity of our method of allowing for k_1 and k_0, we can subtract equations [i] and [ii] to get:

$$dy/dt-dx/dt = \tfrac{3}{2}k_1x^2+k_0x\ .$$

Substituting the value of x from [vii], integrating, and expanding in powers of t, it is found that the fractional error in k_2 so introduced is:

$$\text{Fractional error} = \frac{(6k_1y_0+3k_1x_0-k_0)}{3k_1x_0+2k_0}\ .\ x_0y_0k_2t.$$

The size of this error was checked for runs 31 to 34, and in no case was above 0.3%. Consequently it was assumed to be adequate to obtain k_2 simply by taking the observed slope of x (or y) over each interval between analyses, correcting for the decomposition of hypochlorite if the slope of x is used, and dividing the slope by the mean x times the mean y over the interval. A small correction was applied in accordance with equation [viii]. The mean values of k_2 for each run were:

Run	31	32	33	34	
Temp.	50	50	45	40	°C.
k_2	2.75	2.77	1.64	0.97	$\times 10^{-3}$ min.$^{-1}$(gm-mol./l.)$^{-1}$

These results give an activation energy of 20.8 kcal. In all these runs the ionic strength was 3.79, and the sodium hydroxide concentration was 0.32 *M*. Foerster's results made the activation energy $20\frac{1}{2}$ kcal., in good agreement. However his constant at 50° C. is about 8.3×10^{-4}, but the difference may be due to a different ionic strength. These values of k_2 mean that a decomposing sodium hypochlorite solution will contain about 1/100 as many chlorite ions as hypochlorite ions at 40° C.; this was roughly found. If the constants k_1 and k_2 are written as $Ae^{-E/RT}$, the A factors are fairly similar:

$$k_1 = 2.1\times10^{12}.e^{-24.8\ \text{kcal.}/RT};\quad k_2 = 3.2\times10^{11}.e^{-20.8\ \text{kcal.}/RT}.$$

To summarize these conclusions, it is believed that these results show that (i) the mechanism of Foerster *et al.* via chlorite is well established; (ii) the first stage to chlorite has an activation energy of 24.8 kcal., and is slower than the second stage, which has an activation energy of 20.8 kcal.; (iii) the rates are strongly influenced by the ionic strength; (iv) added sodium hydroxide, carbonate, or chloride changes the rate by changing the ionic strength, but apart from this they exert no specific catalytic effect; and (v) there is a simultaneous unimolecular decomposition to oxygen, which is possibly, but not certainly, uncatalyzed.

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DECOMPOSITION OF SODIUM HYPOCHLORITE: THE CATALYZED REACTION[1]

By M. W. Lister

ABSTRACT

The catalyzed decomposition of sodium hypochlorite has been examined; the catalysts tried were manganese, iron, cobalt, nickel, and copper oxides. It was shown that in no case was the decomposition to chlorate and chloride accelerated, only the reaction to chloride and oxygen. Manganese and iron did not catalyze even the latter reaction, or only to a very small extent; this was in fairly concentrated sodium hypochlorite containing some sodium hydroxide. The manganese and iron are largely oxidized to permanganate and ferrate under these conditions. It was found that copper could catalyze the formation of permanganate and ferrate, and nickel the formation of permanganate. Cobalt catalyzed the reaction going to oxygen, and the rate was proportional to the cobalt added, but little dependent on the hypochlorite concentration; the same is true of nickel. Copper (as reported earlier) gives a catalyzed reaction not far from first order in hypochlorite. The activation energies were measured, and were consistent with the relative catalytic activity of these metals. The mechanism of the reaction is briefly discussed.

The decomposition of sodium hypochlorite is catalyzed by the oxides of transition elements such as cobalt. Qualitatively this was first known a long time ago, but quantitative measurements on the catalysis are much more recent. Howell (3) made a careful study of the catalysis by cobalt oxide. He added the cobalt oxide as a fine, almost colloidal, suspension in water, and measured the rate of oxygen evolution from the vigorously stirred mixture. At fairly low catalyst concentrations (about 2 mgm. cobalt in 60 ml. of solution), he found the rate to be proportional to the catalyst and to the hypochlorite concentrations. The activation energy of the catalyzed reaction was 16.6 kcal./gm-mol. Moelwyn-Hughes (10) was able to calculate that Howell's rate constants are fairly near what one would expect if the catalyst were present as particles of 5×10^{-7} cm. diam., and if every collision with a hypochlorite ion with sufficient energy were effective. Chirnoaga made somewhat similar measurements for cobalt and nickel oxides (1). He found the rate to be independent of the stirring speed, provided this was moderately rapid. His rates were not proportional to the hypochlorite concentration: with nickel oxide they were proportional to $(ClO^-)^{0.47}$ at low concentrations (0.02 to 0.04 M). With cobalt oxide the rate was proportional to $(ClO^-)^{0.9}$. The activation energy was 15.8 kcal. for cobalt oxide, and 16.6 kcal. for nickel oxide. Both Howell and Chirnoaga reported that if the catalyst was washed for a long time till all alkali was removed, it was more active. This may be a peptizing effect due to removal of electrolyte. However all the hypochlorite solutions used contained free alkali. Chirnoaga reported that the order of catalytic activity was Ni > Co > Cu > Fe > Mn, although nickel and cobalt might be expected to be in the reverse order from the activation energies.

Dixon and White (2) examined the conversion of Mn(II) to permanganate by hypochlorite, and noted that copper could catalyze this. Lewis (5, 6) examined cobalt, copper, and iron oxides as catalysts. At fairly high concen-

[1]*Manuscript received November 14, 1955.*
Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario.

trations he found the rate to be independent of the hypochlorite concentration, and it seems difficult to reconcile his results with those of Howell. He was also particularly interested in the effect of adding substances, ordinarily inert, as promoters.

The present author (8) made measurements on the catalysis by copper, during some investigations of the complex copper tellurates and periodates. As these results were obtained under conditions comparable to the measurements reported in this paper, they will be discussed briefly later.

One of the difficulties in interpreting the results of these measurements (either the earlier or the present work) is the uncertainty in the size of the catalytic particles. The apparent gross size is, of course, no certain indication of the true surface area, as pores are probably present. Comparisons with previous rate measurements always contain this element of uncertainty. Consequently the present work was confined to some more limited matters about the reaction. Firstly, although the decomposition to sodium chloride and oxygen is certainly catalyzed, it is not clear whether the decomposition to sodium chloride and chlorate is similarly catalyzed. Secondly, it has sometimes been suggested that qualitatively the mechanism of catalysis is through unstable higher oxides, which are formed, decompose, and are reformed by further oxidation, and so on. However manganese and iron do not have such unstable higher oxides, so their degree of catalytic activity was investigated. Thirdly, the energies of activation of all the catalyzed reactions were measured again. Finally, some further evidence on the dependence on hypochlorite concentration was obtained, which supports Lewis's views at least over a certain range of conditions; but there are several factors which can affect the rate, and a complete study of the matter would require a great many experiments.

EXPERIMENTAL METHOD

The materials used were the same as in the previous paper, with the addition of the salts of various metals used as catalysts. Reagent grade samples of manganese chloride, ferric nitrate, cobalt chloride, nickel chloride, and copper chloride were used. Stock solutions of these salts were made up, and various amounts were pipetted out, and added to well-stirred alkaline sodium hypochlorite. Precipitates of the oxides immediately formed, except with copper. These precipitates were finely divided, but not colloidal; as far as possible the conditions of addition were the same each time. The solutions were then brought to the desired temperature in a thermostat, with continual stirring, and the rate of gas evolution was measured. Samples were taken for analysis from time to time. The apparatus was the same as described in the first paper on the uncatalyzed reaction (9). The analytical methods have been described in another previous paper (7).

The sodium hypochlorite was the same as in the investigation of the uncatalyzed reaction; its ionic strength was 3.79, and it was 0.32 M in sodium hydroxide.

EXPERIMENTAL RESULTS AND CONCLUSIONS

Before describing the quantitative runs, a few qualitative observations might be included. Dixon and White (2) observed that copper catalyzed the

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formation of permanganate. Manganese dioxide is, of course, first formed, starting with Mn(II); and even without copper, permanganate is formed slowly at room temperature. It was noticed that nickel also catalyzed the formation of permanganate, though less efficiently than copper. Sodium chlorite does not oxidize Mn(II) beyond manganese dioxide.

Iron is similarly slowly oxidized to ferrate in the cold, and quite rapidly at 80° C.; as would be expected the reaction goes faster in strongly alkaline solution. Although the ferrate is unstable on boiling, it decomposes only very slowly at 60° C. Copper also accelerates the formation of ferrate, but nickel seems to be unable to do this. The qualitative behavior of copper was described in the paper mentioned earlier (8). As is well known, cobalt and nickel are oxidized to higher oxides by sodium hypochlorite, which are almost completely insoluble in the alkaline solution. Sodium chlorite will not accomplish any of these oxidations.

In the quantitative runs, it is probably simplest to consider each element separately; the results will be given and any conclusions drawn from them before going on to the next element.

Manganese

The data on manganese as a catalyst are given in Table I. The conclusion that must be drawn from these results is that manganese does not catalyze

TABLE I

Run	Temp., ° C.	Mn added, mgm.	Solution volume, ml.	Time, min.	(ClO^-), M	(ClO_2^-), M	(ClO_3^-), M
1	50	3.32	796	0	1.285	0.009	0.122
				286	1.261	0.008	0.128
2	60	3.32	786	0	1.240	—	—
				278	1.171		

Run	Temp., ° C.	Mean (ClO^-), M	Gas rate, ml. N.T.P./min. per liter soln.
1	50	1.273	0.0568
2	60	1.21	0.145

the reaction at all. If we use the same equation that was applied to the uncatalyzed runs (9),

$$-dx/dt = \tfrac{3}{2}k_1x^2+k_0x,$$

where $x = (ClO^-)$,

k_1 = rate constant for first stage of reaction to chlorate,

k_0 = rate constant for reaction to oxygen,

then the results above give for the constants:

Temp.	50	60 ° C.
k_0	4.0	10.7×10^{-6} min.$^{-1}$
k_1	3.25	10.75×10^{-5} (gm-mol./l.)$^{-1}$ min.$^{-1}$

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By "reaction to chlorate" is meant the reaction

$$3OCl^- \rightarrow ClO_3^- + 2Cl^-$$

of which the first step is

$$2OCl^- \rightarrow ClO_2^- + Cl^-.$$

This is the slow rate determining step, and k_1 is its rate constant. By "reaction to oxygen" is meant the reaction

$$2OCl^- \rightarrow 2Cl^- + O_2.$$

This was found to be a first order reaction, and k_0 is its rate constant. These reactions are the ones meant in all references in later sections to "reaction to chlorate" or "reaction to oxygen".

The ionic strength of the solution after addition of catalyst was 3.78. The k_0 values are just about right for this ionic strength, and make the energy of activation 21 kcal., in agreement with results obtained earlier. The k_1 values are a little low, but certainly show that manganese does not catalyze the reaction under these conditions. The reason for the difference between these results and those of Chirnoaga probably lies in the higher concentration and sodium hydroxide content of the present solutions. Chirnoaga's sodium hypochlorite was only 0.042 *M*, and his manganese dioxide was 0.0061 *M*, so an appreciable fraction of the hypochlorite could be used up in oxidizing the manganese; indeed over half of the decomposition that he observed could be explained in this way. However the present results do show that manganese is not catalytic in concentrated solutions of hypochlorite.

Iron

The data on iron as a catalyst are given in Table II. Again we can treat these results by the method for uncatalyzed runs, which gives values for the rate constants as shown below. Values of k_1 from the chlorate analyses are also included, as these help to distinguish the catalytic effect (if any) on the two reactions. It may be added that constants obtained from the chlorate analyses have the advantage of not needing a value of the gas rate for their

TABLE II

Run	Temp., °C.	Fe added, mgm.	Time, min.	(ClO^-), *M*	(ClO_2^-), *M*	(ClO_3^-), *M*
3	50	3.84	0	1.256	0.008	0.131
			439	1.216	0.008	—
			1157	1.158	0.008	0.162
			1391	1.138	0.008	—
4	60	3.84	0	1.126	0.010	0.167
			462	1.030	—	—
			1377	0.873	0.009	0.246

Run	Temp., ° C.	Mean (ClO^-), *M*	Gas rate, ml. N.T.P./min. per liter soln.
3	50	1.19	0.070
4	60	1.11	0.159
		0.90	0.114

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calculation; but against this must be set the fact that the chlorate concentrations are obtained by the difference of two analyses, one of which does not have a very easily observed end point. The values of the constants are:

Temp.	50	60 ° C.
k_0	5.2	12.0×10^{-6} min.$^{-1}$
k_1	3.59	11.6×10^{-5} (gm-mol./l.)$^{-1}$ min.$^{-1}$
k_1 (from chlorate)	3.70	11.5×10^{-5} (gm-mol./l.)$^{-1}$ min.$^{-1}$

There may be some catalytic effect on the reaction to oxygen, but it is very slight. As compared with, for instance, cobalt, the iron is at most 1/200 times as active as a catalyst. There is no sign of any catalysis of the chlorate reaction: the uncatalyzed rate constants at this ionic strength (3.79) are 3.61×10^{-5} at 50° C., and 11.4×10^{-5} at 60° C. We must add, of course, that these conclusions only apply to the conditions of these experiments; that is to say in fairly high hypochlorite concentrations, moderate alkalinity, and not too high temperatures; but under these conditions iron does not catalyze the chlorate reaction, and it catalyzes the oxygen reaction very slightly, if at all.

Cobalt

The data obtained are given in Table III. Cobalt, of course, catalyzes the oxygen reaction, but its effect on the chlorate reaction is not so obvious. The rigorous determination of k_1 from these data is not easy because of the high

TABLE III

Run	Temp., ° C.	Co added, mgm.	Time, min.	(ClO^-), *M*	(ClO_2^-), *M*	(ClO_3^-), *M*
5	50	3.16	0	1.246	0.001	0.134
			488	1.074	—	0.146
			1262	0.854	0.003	0.160
6	50	1.58	0	1.229	0.002	0.139
			440	1.109	0.004	0.150
			1338	0.924	0.002	0.167

Run	Temp., ° C.	Mean (ClO^-), *M*	Gas rate, ml. N.T.P./min.	Co added, mgm.
5	50	1.235	2.47	3.16
		1.065	2.35	
6	50	1.17	1.24	1.58
		1.08	1.02	
7	50	0.91	0.87	1.58
		0.50	0.81	
8*a*	30	1.25	0.51	3.16
8*b*	40	1.23	1.08	3.16
8*c*	50	1.18	2.46	3.16
8*d*	45	1.03	1.87	3.16
9*a*	30	1.25	0.225	3.16
9*b*	40	1.23	0.59	3.16
9*c*	50	1.19	2.48	3.16
9*d*	45	1.05	1.84	3.16
9*e*	40	0.98	1.16	3.16
9*f*	35	0.94	0.71	3.16
9*g*	30	0.91	0.49	3.16

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gas rate. However a reasonable approximation can be obtained by observing the total rate of decomposition between any two analyses; we then put:

$$\text{total rate} = \text{rate to oxygen} + \text{rate to chlorate}$$

and:

$$\text{rate to chlorate} = \tfrac{3}{2}k_1\bar{x}^2$$

where $\bar{x}$ is now the mean hypochlorite concentration between the two analyses. Hence k_1 can be calculated. The error from taking this approximate equation, and not an integrated equation, is small. This was checked by integrating the above equation for various plausible expressions for the dependence of the rate to oxygen on x; then the approximate k_1 could be expressed in terms of the true k_1 and known quantities such as x or the time. This enables an estimate of the error in the approximate k_1 to be made, and in the actual runs this never exceeded 1%. Although k_1 could have been obtained from these integrated equations, they were rather cumbersome expressions; and it was felt that the approximate equation allowed for the actual observed gas rate in a more direct manner.

Considering first runs 5 and 6, we get the following values of k_1, averaged over the entire run (ionic strength 3.79):

Run	k_1 from ClO^-	k_1 from ClO_3^-
5	3.74 $\times10^{-5}$	3.68 $\times10^{-5}$ (gm-mol./l.)$^{-1}$ min.$^{-1}$
6	3.66	3.61

These values are near enough to the uncatalyzed rate constant (3.61×10^{-5}) to be within the experimental error. Hence cobalt does not catalyze the chlorate reaction to a detectable extent.

If we look at the oxygen reaction, a comparison of runs 5 and 6 shows that at the same hypochlorite concentration, the rate is proportional to the cobalt added. This agrees with all previous work. The dependence on hypochlorite is more obscure, but a few tentative remarks can be made. Firstly, it is difficult to distinguish, during any one run, an 'aging' effect in the catalyst from a dependence of the rate on the hypochlorite concentration. Howell avoided this difficulty in some of his runs by filtering off a catalyst at the end of a run and re-using it; he found its activity had fallen a few per cent. The 'aging' is presumably due to agglomeration of the catalyst particles, thereby reducing their surface area; or to poisoning of the catalyst by impurities. Howell found that typical catalyst poisons had no effect, so probably changes were due to agglomeration. The following observation supports this view. It was found that if a catalyst was used for some time, then left overnight without stirring, and stirring was started next day at a fairly low temperature, then the rate of gas evolution was low (run 9*a* at 30° C.). If the temperature was increased in steps, then the rate rose towards what was found for fresh catalyst, and at 50° C. the catalyst had recovered (runs 9*b*, 9*c*). The simplest explanation is that the vigorous gas evolution at 50° C. had broken up the agglomerated particles. If the temperature was subsequently decreased, the fresh catalyst rate was more or less maintained (compare runs 8*a*, 9*g*), at least for long enough

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to observe the gas rate. Hence it is impossible to say with any confidence whether the fall in rate during runs 5 and 6 is due to aging of catalyst or fall in (ClO^-). However run 7 does provide some evidence on this, as the two rates in this run were measured on the same solution to which water was added between the measurements. The rate only fell 7% for a decrease in hypochlorite concentration of 45%. Similarly a comparison of runs 5, 8*c*, and 9*c* shows nearly the same rates over a moderate range of concentration. On the whole it seems fair to conclude that, under the conditions of these experiments, the rate is very little dependent on hypochlorite, in agreement with Lewis.

This in no sense contradicts Howell's results for his experimental conditions. The difference does not lie apparently in the concentrations used, which were much the same as in the present work. The difference is probably in the method of preparation of his catalyst: per milligram his catalyst was about three times as active as that in Lewis's or the present work. Even so the degree of difference seems surprising, and the matter cannot be regarded as settled.

Runs 8 and 9 give the temperature dependence of the rate; they make the energy of activation 15.9 (±0.5) kcal./gm-mol. This is to be compared with 15.8 kcal. found by Chirnoaga, 16.6 kcal. by Howell, and (in effect) 13.3 kcal. by Lewis.

TABLE IV

Run	Temp., ° C.	Ni added, mgm.	Time, min.	(ClO^-), *M*	(ClO_2^-), *M*	(ClO_3^-), *M*
10	40	3.39	0	1.369	0.006	0.095
			164	1.352	0.004	0.104
			409	1.329	0.004	0.106
			1228	1.266	0.004	0.112
11	50	3.39	0	1.243	0.003	0.115
			366	1.173	0.004	0.125
			1322	1.000	0.005	0.145
12	60	3.39	0	0.960	0.005	0.148
			320	0.833	0.003	0.164
13	50	0.85	0	1.315	0.008	0.116
			230	1.280	0.008	0.123

Run	Temp., ° C.	Mean (ClO^-), *M*	Gas rate, ml. N.T.P./min.	Ni added, mgm.
10	40	1.36	0.47	3.39
		1.33	0.52	
		1.27	0.50	
11	50	1.23	1.23	3.39
		1.16	1.11	
		1.02	1.17	
12	60	0.95	2.63	3.39
		0.84	2.65	
13	50	1.30	0.321	0.85
		1.28	0.333	
14	50	0.82	1.17	3.39
		0.81	1.16	

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Nickel

The data on nickel are given in Table IV. The first point to settle is whether nickel catalyzes the chlorate reaction. If we calculate the rate constant, k_1, as for cobalt, the result is:

Run	Temp., ° C.	k_1 from ClO^-	k_1 from ClO_3^-
10	40	1.35 $\times 10^{-5}$	1.29 $\times 10^{-5}$ (gm-mol./l.)$^{-1}$ min.$^{-1}$
11	50	3.52	3.62
12	60	10.5	13.0

The experimental error at 40° C. is fairly large, as an error of 0.001 in the hypochlorite concentration would alter k_1 by nearly $2\frac{1}{2}\%$. However it seems possible to conclude that within the experimental error, nickel does not catalyze the chlorate reaction. Runs 11 and 13 show that the rate is proportional to the nickel added, in agreement with all previous work.

The dependence of the catalyzed rate on hypochlorite concentration is best seen from runs 11, 12, and 14. Over the range of concentrations examined (0.81 to 1.23 *M*) there was no observable change in the catalyzed rate with hypochlorite concentration. Again this does not mean that under other conditions such a dependence might not be found. Chirnoaga found the rate to be proportional to $(ClO^-)^{0.47}$, at low concentrations; this is a lesser degree of dependence on concentration than he found with cobalt.

The mean gas rates at about 1 *M* hypochlorite, with 3.39 mgm. of nickel, at various temperatures are:

Temp.	40	50	60	° C.
Gas rate	0.50	1.17	2.64	ml./min.

These make the activation energy 17.2 kcal./gm-mol. A little (about 4%) of the total rate can be attributed to the uncatalyzed reaction, and if allowance is made for this, the activation energy is reduced to 17.1 kcal.

Copper

In another paper (8), the writer has given details of the effect of copper as a catalyst. The only point that will be dealt with here is whether copper catalyzes the reaction to chlorate. Table V gives the experimental results. From these results we can calculate k_1, using interpolated values of the rate of oxygen evolution at the appropriate hypochlorite concentration. The values so obtained are:

Run	15	16	17(0–1162′)	17(1162–2921′)	18	19	
k_1 from (ClO^-)	3.88	3.61	3.35	3.65	3.82	3.44	$\times 10^{-5}$
k_1 from (ClO_3^-)	4.08	—	3.82	3.60	—	—	$\times 10^{-5}$

The long run (17) was arbitrarily divided into two parts for this calculation as the range of concentration is large, but similar results would be obtained from other time intervals in this run. The accuracy of k_1, as obtained above, is not very great, as small changes in the analytical results would give relatively large changes in k_1. However it seems reasonably certain from these results that copper does not catalyze the reaction to chlorate.

As mentioned above, the dependence of rate on concentration has been reported by the writer in an earlier paper on another aspect of the chemistry

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TABLE V

Run	Cu added, mgm.	Time, min.	(ClO^-), M	(ClO_3^-), M
15	3.92	0	1.250	0.120
		196	1.094	0.1255
16	3.92	0	1.018	—
		$57\frac{1}{2}$	0.979	—
17	1.96	0	1.201	0.124
		426	1.058	0.141
		1162	0.8325	0.157
		2595	0.500	—
		2921	0.4355	0.170
18	1.96	0	1.240	—
		543	0.940	—
19	1.96	0	0.982	—
		493	0.839	

Run	Mean (ClO^-), M	Gas rate, ml. N.T.P./min.
15	1.23	6.39
16	1.01	5.67
	0.99	5.33
17	1.05	2.42
	0.81	2.12
	0.71	1.97
	0.44	1.45
18	1.09	2.75
19	0.95	2.25
	0.84	2.00

of copper. Briefly, it was found that the rate could best be represented by an equation of the form:

$$\text{rate} = (\text{Cu})\{a+b(ClO^-)\}$$

where a and b are constants, and b is larger than a. The over-all energy of activation was 15.5 kcal./gm-mol.

GENERAL REMARKS

Comparison of the results with various metals enables us to make a few general comments on these reactions. In the first place, it was found that in no case was the chlorate reaction catalyzed (or only to a very small extent). This suggests that the mechanism of the catalysis is through oxidation of the metal to a higher oxide, which then loses oxygen, and is subsequently re-oxidized, and so on. The inertness of iron and manganese where there is no unstable higher oxide supports this view. Unfortunately, if we calculate the rate of decomposition of the higher oxide which would provide the observed gas evolution, it seems to be impossibly high. For instance in run 5, 5.4×10^{-5} gm-atoms of cobalt gave 2.2×10^{-4} gm-atoms of oxygen per minute. If the

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change is from Co(III) to Co(II), this means that the half life of the oxidized cobalt atom is only 5.2 sec., even if all the Co(II) is instantaneously re-oxidized. As $Co_2O_3.H_2O$(or CoO.OH) is reported (4) to have been isolated, and to be stable on drying at 150° C., the above theory of the reaction seems to be untenable. Similar remarks apply, though with somewhat less force, to nickel and even to copper. Of course, we cannot entirely dismiss the possibility that the reaction is due to some still higher oxide, but this is hypothetical.

The only alternative seems to be that the reaction goes in the stages (M is any catalytic metal):

$$\text{(i)}\quad 2MO + ClO^- \rightarrow M_2O_3 + Cl^-$$
$$\text{(ii)}\quad M_2O_3 + ClO^- \rightarrow M_2O_3.ClO^- \text{ (adsorbed)}$$
$$\text{(iii)}\quad M_2O_3.ClO^- \rightarrow 2MO + Cl^- + O_2$$

This, of course, was realized by earlier workers on the reaction. If the reaction rate is independent of the hypochlorite concentration, then (iii) must be the slow stage, and much the same amount of hypochlorite must be adsorbed in (ii) over a range of concentration. While there is really no direct evidence of this, the simplest picture is one in which the entire catalyst surface is kept covered with adsorbed hypochlorite ions at the rather high concentrations actually used. If the catalyst surface is not completely covered, it is impossible to predict what the reaction kinetics would be without knowing the dependence of adsorption on concentration. Only if the adsorption were proportional to the hypochlorite concentration could we expect a first order reaction; this might happen in dilute solutions. Thus cobalt and nickel, at the concentrations used, behave as though the catalyst were fairly completely covered with adsorbed ions. Copper is entirely, or nearly entirely, in solution; and the reaction, as might be expected, is not far from being first order in both copper and hypochlorite. Manganese and iron do not catalyze the reaction, and this is at least in part attributable to their oxidation to stable states.

It is interesting to compare the rates with the activation energies. At 50° C., 10^{-4} gm-atoms of metal in 1 *M* sodium hypochlorite would give gas rates as follows:

Metal	Co	Ni	Cu	
Rate	4.0	2.0	7.4	ml./min.
Activation energy	15.9	17.1	15.5	kcal./gm-mol.

Thus the rate increases as the activation energy decreases. The rate with nickel seems somewhat large compared with the others, as the activation energy is over 1 kcal. larger.

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THE REACTION BETWEEN CYANATE AND HYPOCHLORITE[1]

By M. W. Lister

ABSTRACT

The reaction between sodium hypochlorite and potassium cyanate in the presence of sodium hydroxide has been examined. The main products are chloride, and carbonate ions and nitrogen; but, especially if much hypochlorite is present, some nitrate is formed as well. The rate of reaction is proportional to the cyanate and hypochlorite concentrations, but inversely proportional to the hydroxide concentration: the rate constant is 5.45×10^{-4} min.$^{-1}$ at 65° C., at an ionic strength of 2.2. The rate constant increases somewhat as the ionic strength rises from 1.7 to 3.5. The effect of temperature makes the apparent activation energy 25 kcal./gm-molecule. The kinetics of the reaction suggest that the slow step is really a reaction of hypochlorous acid and cyanate ions, and possible intermediate products of this reaction are suggested. Allowing for the different extent of hydrolysis of hypochlorite at different temperatures, the true activation energy is found to be 15 kcal./gm-mol., which is consistent with the observed rate of reaction.

In a recent paper (4), the writer reported some observations on the oxidation of potassium cyanate by sodium hypochlorite in the presence of small amounts of alkali. It was found that there was at first a marked induction period, after which a rapid reaction took place which approximately followed the equation:

$$2OCN^- + 3OCl^- + H_2O \rightarrow 2HCO_3^- + 3Cl^- + N_2.$$

The time required for the rapid reaction to develop depended on the concentration of sodium hydroxide, and was much less at low hydroxide concentrations. It was suggested that the acceleration of the reaction was due to the liberation of large amounts of hypochlorous acid, which oxidized the cyanate rapidly. It has since been found that the pH when the reaction accelerates is about 10. This is much too high a pH for cyanic acid to be formed, but would be reasonable for the liberation of hypochlorous acid. The reaction produces bicarbonate ions which are acid enough to lower the pH below this critical value.

A slow reaction took place even in the presence of excess alkali, and it is this reaction that is the subject of the present paper. The products are carbonate and chloride ions and nitrogen, at least in the predominant reaction. It is hardly likely that a complicated reaction of this sort would go in one step; and it was hoped that a knowledge of the kinetics would help to elucidate the mechanism, for there are no very obvious intermediate products. It is thought that the present work provides a fair amount of information on the reaction, though a detailed mechanism cannot yet be given.

EXPERIMENTAL METHOD AND RESULTS

The reagents used in these experiments were as follows. The same potassium cyanate was used as in the preceding paper (4). Sodium hypochlorite solution

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was made in the usual way by passing chlorine into cold aqueous sodium hydroxide. A reagent grade of potassium hydroxide was used to control the hydroxide concentration. In some runs reagent grade sodium chloride or carbonate was added to alter the ionic strength.

The general procedure in any run was as follows. Solutions of potassium cyanate with added potassium hydroxide were made up as required. To these were added varying amounts of sodium hypochlorite solution, and in most runs solid sodium chloride or carbonate also, to control the ionic strength. The reaction mixture was contained in a 1 liter flask, fitted with (i) a mercury sealed stirrer, (ii) a side arm, normally closed, for taking samples, and (iii) a capillary lead to a water jacketed gas burette. The flask was immersed in a water thermostat of conventional design, whose temperature was controlled to $\pm 0.1°$ C.

During a run samples were taken at intervals and analyzed. Three sorts of analysis were used to follow the reaction: these were for (i) hypochlorite, (ii) cyanate, and (iii) total alkalinity. In addition the stock hypochlorite solution was analyzed for chlorite, chlorate, hydroxide, and carbonate, as it was necessary to know its ionic strength. The methods, except for cyanate and total alkalinity, have been described in an earlier paper (5). These are all well known titrations with minor modifications. To determine cyanate, a sample was run into 20 ml. of 3% hydrogen peroxide, to destroy hypochlorite. The mixture was acidified, and heated nearly to boiling to convert all cyanate to ammonium ions. Excess alkali was then added, and the ammonia distilled into a known amount of standard sulphuric acid, and the remaining acid was titrated in the usual way. 'Total alkalinity' was determined by the following procedure. A sample was pipetted out and titrated with standard sulphuric acid. Near the end point the solution was heated to boiling, and acid was run in until the green color of bromcresol green, which was used as indicator, was maintained even in the hot solution. At this point all hydroxide and carbonate have been titrated (the latter to carbonic acid), and the cyanate just converted to ammonium ions and carbon dioxide:

$$2KOCN + 2H_2SO_4 + 2H_2O \rightarrow K_2SO_4 + (NH_4)_2SO_4 + 2CO_2.$$

In one run the reaction of sodium chlorite and potassium cyanate was examined. This was done because hypochlorite always contains a small amount of chlorite, and it seemed possible that a reaction of this sort might contribute appreciably to the total rate. The procedure was the same except that a solution of recrystallized sodium chlorite was used.

The results are given in Tables I to V, which are arranged as follows. Table I gives the main series of runs, which were made to determine the kinetics of the reaction. All these runs were at 65° C., and an ionic strength of 2.2. Table II gives the results of varying the ionic strength, and Table III the results of varying the temperature. The observations on gas evolution are given in Table IV. Finally the single run with chlorite is given in Table V.

TABLE I

All runs at 65° C. and an ionic strength of 2.2

Run	Time, min.	(ClO^-), *M*	(OCN^-), *M*	Total alkalinity, *N*	(NaOH), *M*
1	0	0.2495	0.313	0.913	0.286
	41	0.235	0.299	—	
	111	0.2005	0.284	0.875	
	201½	0.1645	—	—	
	317	0.1285	—	0.815	
	361	0.116	0.234	—	
2	0	0.461	0.304	0.965	0.357
	65	0.419	0.285	0.929	
	114	0.387	—	0.915	
	190	0.347	0.250	0.895	
	279	0.2925	—	0.873	
	300	0.243	0.194	0.856	
3	0	0.715	0.307	1.010	0.396
	52	0.661	0.292	0.988	
	104	0.615	0.265	0.959	
	185	0.535	0.232	0.929	
	277	0.4735	0.200	0.900	
	353	0.424	0.167	0.876	
4	0	0.2555	0.628	1.536	0.280
	42	0.2115	—	1.504	
	124	0.1455	0.561	1.495	
	190	0.104	0.533	1.465	
	261	0.071	0.513	1.456	
	317	0.0505	0.505	1.442	
5	0	0.3005	1.129	2.553	0.296
	45½	0.213	1.040	2.312	
	91½	0.1485	0.984	2.273	
	176½	0.063	0.937	2.258	
	254	0.0215	0.915	2.255	
6	0	0.299	0.106	0.526	0.314
	200	0.268	0.0925	0.512	
	330	0.250	0.080	0.496	
7	0	0.2955	0.329	1.561	0.245
	66	0.257	0.305	1.546	
	150	0.2085	0.281	1.512	0.329 *M*
	272	0.1545	0.250	1.484	Na_2CO_3
	346	0.1275	0.233	1.470	
8	0	0.294	0.328	1.192	0.536
	67	0.270	0.318	1.174	
	177	0.239	0.297	1.160	
	312	0.2035	0.280	1.143	
	383	0.192	—	—	
9	0	0.293	0.321	1.796	1.13
	207	0.267	0.307	1.760	
	315	0.2485	—	—	
	374	0.2385	0.290	1.748	
10	0	0.2835	0.317	0.838	0.205
	79	0.2285	0.286	0.813	
	147	0.1905	0.262	0.795	
	229	0.1445	0.237	0.766	

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TABLE II

All runs are at 65° C.

Run	Ionic strength	Time, min.	(ClO^-), *M*	(OCN^-), *M*	(NaOH), *M*
11	1.7	0	0.453	0.382	0.295
		61	0.4075	0.361	
		133	0.3625	0.327	
		185	0.3295	0.305	
		280	0.270	0.271	
		345	0.2405	0.242	
12	2.0	0	0.450	0.166	0.271
		77	0.416	0.159	
		183	0.3755	0.138	
		298	0.340	0.115	
		368	0.327	0.100	
13	2.9	0	1.037	0.324	0.503
		53½	0.977	0.303	
		117	0.900	0.272	
		205	0.803	0.235	
		289	0.731	0.198	
14	3.5	0	0.211	0.355	0.349
		100	0.1715	0.332	
		227	0.1305	0.308	
		299	0.115	0.301	

TABLE III

All runs at an ionic strength of 2.2

Run	Temp., ° C.	Time, min.	(ClO^-), *M*	(OCN^-), *M*	(NaOH), *M*
15	55	0	0.294	0.322	0.283
		124	0.265	0.304	
		265	0.2385	0.293	
		403	0.2165	0.286	
16	75	0	0.252	0.298	0.325
		49	0.193	0.277	
		112	0.135	0.245	
		174	0.0945	0.229	
		256	0.059	0.2035	
17	50	0	0.468	0.287	0.386
		60	0.459	—	
		125	0.453	—	
		450	0.425	—	
		1129	0.360	—	
		1606	0.3145	—	
		1620	0.3125	—	
		2548	0.257	—	
		3016	0.2325	0.159	

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TABLE IV

Run	Time interval, min.	Gas rate, gm-atoms/min. per liter soln.	Run	Time interval, min.	Gas rate, gm-atoms/min. per liter soln.
1	221–241	1.55×10^{-4}	11	35–53	2.32×10^{-4}
	322–352	1.29		147–180	1.87
2	25–37	2.83	12	204–240	0.80
	90–111	2.16		335–363	0.66
3	19–35½	3.75	13	16–30	4.21
	78–94	3.42		76–91	3.55
				223–244	2.76
4	131–151	2.97			
	295–315	2.22	14	236–276	1.32
				304–323	1.27
5	35–45	6.13			
	182–197	3.77	15	274–295	0.45
6	285–330	0.32			
7	164–187	2.30			
	323–343	1.68			
8	82–117	0.87			
	196–236	0.71			
9	215–313	0.81			
10	96–116	2.55			
	160–180	2.56			

TABLE V

Run	Ionic strength	Temp., °C.	Time, min.	(ClO_2^-), *M*	(OCN^-), *M*	(NaOH), *M*
18	2.2	98	0	0.311	0.300	0.191
			34	0.308		
			240	0.251		
			310	0.220		

DISCUSSION OF RESULTS

Although the reaction approximates to

$$2OCN^- + 3OCl^- + 2OH^- \rightarrow 2CO_3^{--} + 3Cl^- + N_2 + H_2O$$

the amounts of cyanate and hypochlorite disappearing do not agree at all closely with this equation. In general more hypochlorite reacts than would be expected. Part of this must be due to the spontaneous decomposition of hypochlorite to chlorate and chloride, but this can only account for part of the discrepancy. The rate of gas evolution is also generally lower than is required by this equation. The most plausible secondary reaction is probably this:

$$OCN^- + 4OCl^- + 2OH^- \rightarrow CO_3^{--} + 4Cl^- + NO_3^- + H_2O.$$

Indeed it is difficult to suggest any other simple compound of nitrogen, except

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possibly nitrous oxide, that might reasonably appear in this reaction mixture, and that would not be oxidized further.

The possibility of nitrous oxide formation was examined by collecting the gas evolved in a special gas burette, at the top of which was a coil of wire that could be heated. Hydrogen was added to the gas, and the wire heated to convert any nitrous oxide to nitrogen and water, and any oxygen to water. Then excess oxygen was added, and the wire was heated again. From the volumes at the various stages of this procedure it is possible to determine how much oxygen and nitrous oxide was present in the original gas. A little oxygen was detected (from decomposition of hypochlorite), but no nitrous oxide, within the experimental error.

Support for the suggestion that nitrate was formed was provided in two ways. First, the reaction mixture from a run with high hypochlorite was treated with enough 3% hydrogen peroxide to destroy the remaining hypochlorite ions. The mixture was then made very acid with concentrated sulphuric acid, and boiled. This removes any cyanate and the excess hydrogen peroxide, but the main object of this procedure was to remove chlorate. The boiling was continued until all chlorine and chlorine dioxide had boiled out of the solution, and addition of more sulphuric acid gave no further yellow color. After the solution was cooled, it was tested for nitrate by (i) the 'brown ring' test with ferrous sulphate and concentrated sulphuric acid, and (ii) 'nitron' acetate solution (7). The second test was applied both to the solution directly after it had been cooled, and to a portion of it which had been neutralized with sodium bicarbonate and then made just acid with acetic acid. Both tests gave a strong reaction for nitrate. Secondly, the amounts of substances appearing and disappearing agreed, roughly, with this secondary reaction. This second line of evidence is not very strong, as we are dealing with small differences in the analyses, or in the rates of gas evolution. The gas evolution itself can be easily measured, but there is always uncertainty as to whether this represents the true rate of reaction to nitrogen, because some of the gas can remain in solution. There was always some lag in the gas evolution at first (as has been noticed in other similar reactions), presumably because the concentration of gas in solution was building up. However after the reaction has been running for some time, the rate of gas evolution must be close to the true rate of reaction.

The calculations which were made to test the suggestion of this secondary reaction were as follows. Suppose we have $2a$ gm-molecules of cyanate reacting by the first reaction:

$$2OCN^- + 3OCl^- + 2OH^- \rightarrow 2CO_3^{--} + 3Cl^- + N_2 + H_2O \qquad \text{I}$$

and b gm-molecules by the second:

$$OCN^- + 4OCl^- + 2OH^- \rightarrow CO_3^{--} + 4Cl^- + NO_3^- + H_2O \qquad \text{II}$$

i.e. $2a$ gm-molecules of cyanate react with $3a$ gm-molecules of hypochlorite by the first reaction, etc. Then the total changes involved would be:

OCl^-: $-3a-4b$; OCN^-: $-2a-b$; total alkalinity: $-2a-2b$; nitrogen (gm-atoms): $2a$.

As the analyses for hypochlorite and cyanate were probably the most reliable,

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values of a and b were obtained from them with the results in Table VI. Table VI also makes allowance for the amount of hypochlorite reacting to

TABLE VI

Run	Change in (OCl^-)	Change in (OCN^-)	Corrn. to OCl^-	Corrected change in (OCl^-)	a	b	b/a	Change in total alkalinity	
								Obs.	Calc.
1	0.1335	0.079	0.002	0.1315	0.0369	0.0052	0.14	0.11	0.084
2	0.228	0.110	0.008	0.220	0.0440	0.0220	0.50	0.109	0.132
3	0.291	0.140	0.019	0.272	0.0576	0.0248	0.43	0.134	0.165
4	0.205	0.123	0.001	0.204	0.0576	0.0078	0.14	0.094	0.131
5	0.279	0.214	0.001	0.278	0.115	(−.017)	—	0.30	0.23
6	0.049	0.026	0.004	0.045	0.0118	0.0024	0.20	0.030	0.028
7	0.168	0.096	0.0025	0.1655	0.0421	0.0086	0.20	0.091	0.101
8	0.0905	0.048	0.003	0.0875	0.0209	0.0062	0.29	0.049	0.054
9	0.0545	0.031	0.004	0.0505	0.0147	0.0016	0.11	0.048	0.033
10	0.139	0.080	0.0015	0.1375	0.0365	0.0070	0.19	0.072	0.087

give chlorate and chloride, which is calculated using a rate constant of 11×10^{-5} (gm-mol./l.)$^{-1}$ min.$^{-1}$. This constant is obtained from results of the writer (6) on this reaction. If x is the concentration of hypochlorite ion, then the rate of the reaction to chlorate is given by

$$-dx/dt = \tfrac{3}{2}k_1x^2$$

where k_1 is the rate constant. The value of x used was the average over the period investigated; that is, the correction used was:

$$\text{correction to hypochlorite used up} = \tfrac{3}{2}k_1[(x_{\text{initial}}+x_{\text{final}})/2]^2.\ (\text{time}).$$

The correction is small enough for this to be sufficiently accurate.

The agreement between the observed and calculated changes in the total alkalinity is very moderate; but we are, of course, dealing with small differences between large quantities. However the results in Table VI do provide some support for the suggested secondary reaction.

Table V shows that there is a slow reaction of chlorite and cyanate ions, but this is quite slow even at 98° C., and with 0.2 to 0.3 M chlorite present. As the chlorite present in hypochlorite from its decomposition is only about $\frac{1}{2}\%$ of the hypochlorite (6), the reaction of chlorite and cyanate is much too slow to contribute appreciably to the total reaction.

Turning to the gas rates, we see that these are generally lower than they would be if all the nitrogen from the cyanate were evolved as gas. If the alternative reaction is as suggested above, then the ratio of the rate of gas evolution (in gm-atoms/min.) to the rate of disappearance of cyanate would be $2a/(2a+b)$. Table VII(a) gives the results of such a comparison. The rates of cyanate disappearance were obtained by plotting the cyanate analyses and drawing smooth curves through them: the rates were read off these smoothed curves. Again there is moderate agreement, but on the whole the gas rates support the reaction proposed above.

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TABLE VII

	Run	Time, min.	Gas rate, gm-atoms/min. per liter soln.	Cyanate rate, gm-mol./liter per min.	b/a	Gas rate calc.
(*a*)	1	221–241	1.55×10^{-4}	2.0×10^{-4}	0.14	1.85×10^{-4}
		322–352	1.29	1.5		1.4
	2	25–37	2.83	2.9	0.50	2.35
		90–111	2.16	2.5		2.0
	3	19–35½	3.75	4.0	0.43	3.3
		78–94	3.42			
	4	131–151	2.97	4.0	0.14	3.7
		295–315	2.22	2.4		2.25
	5	35–45	6.13	—	0	—
		182–197	3.77	4.5		4.5
	6	285–330	0.32	0.5	0.20	0.45
	7	164–187	2.30	2.5	0.20	2.3
		323–343	1.68	2.1		1.9
	8	82–117	0.87	1.4	0.29	1.2
		196–236	0.71	1.2		1.05
	9	215–313	0.81	0.8	0.11	0.75
	10	96–116	2.55	3.2	0.19	2.9
		160–180	2.56	3.0		2.7
(*b*)	11	35–53	2.32	3.4	0	3.4
		147–180	1.87			
	12	204–240	0.80	1.5	0.21	1.35
		335–363	0.66			
	13	16–30	4.21	4.9	0.58	3.8
		76–91	3.55	4.6		3.5
		223–244	2.76	4.2		3.2
	14	235–276	1.32	1.45	0.28	1.25
		304–323	1.27			
	15	274–295	0.45	0.75	0.27	0.65

The values of b/a are of some interest. Many of these are in the neighborhood of 0.1 to 0.2, which means that the reaction to nitrate is a minor one but not negligible. In runs 2 and 3, when (ClO^-) was high, so was b/a; thus a high concentration of hypochlorite favors, as might be expected, the more extreme oxidation to nitrate. Conversely, when (OCN^-) was very high in run 5, the ratio b/a was diminished. The apparent negative value of b in this run is presumably due to experimental error. When the sodium hydroxide concentration is varied, b/a does not change in any systematic manner, so sodium hydroxide does not affect the relative chances of the reaction going to nitrogen or nitrate. Thus, so far as they go, these values of b/a are consistent with the suggested reactions.

If we now examine the rates of reaction in runs 1 to 10, we find from runs 1 to 3 that the rate is at least roughly proportional to (OCl^-), if the other concen-

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trations are the same. Similarly from runs 1, 4, 5, and 6, the rate is roughly proportional to (OCN^-). If we obtain (OH^-) from the total alkalinity at the start, we find from runs 1, 7, 8, 9, and 10 that the rate is roughly inversely proportional to the hydroxide concentration. Then if x is the hypochlorite concentration (initially x_0); y is the cyanate concentration (initially y_0); and z is the hydroxide concentration (initially z_0); these results would mean that

$$-dx/dt = k^*xy/z$$

where k^* is a constant. If the first reaction (I above) is followed, we should write

$$-dx/dt = 3kxy/z$$

where k is the correct rate constant, since three hypochlorite ions are used up in the reaction, but presumably only one in the first stage. We also have:

$$2\ dx/dt = 3\ dy/dt = 3\ dz/dt.$$

These equations integrate to give:

$$[i] \qquad -kt = \frac{1}{2x_0-3y_0}\left[(\tfrac{2}{3}x_0-z_0)\ln\frac{x}{x_0}+(z_0-y_0)\ln\frac{(2x-2x_0+3y_0)}{3y_0}\right].$$

The best way to check this equation is to calculate kt for various values of x, and then to fit the experimental points to this curve for each run by taking some value of k. This was done (see Fig. 1), and in general an adequate fit was

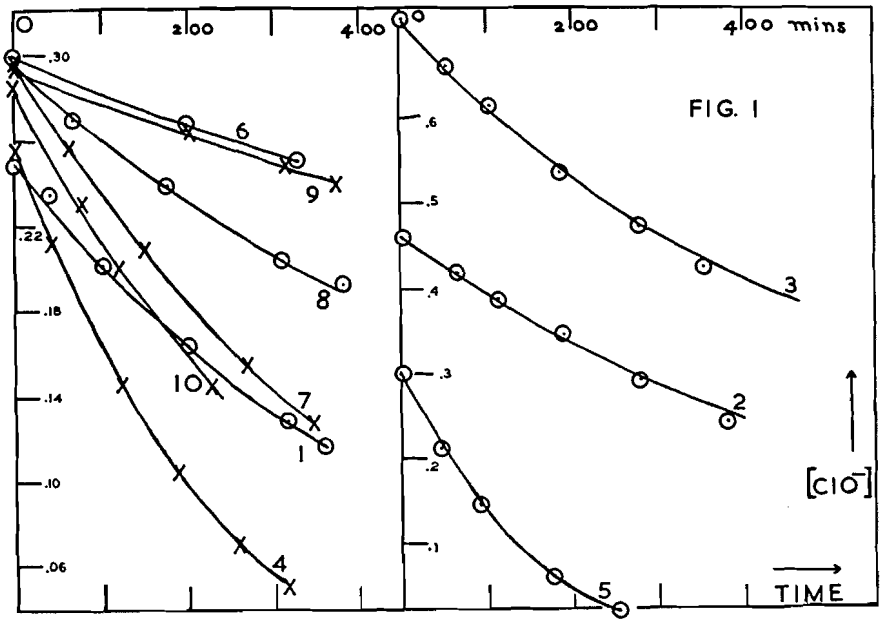

FIG. 1. Comparison of hypochlorite concentrations calculated by equation [i] with experimental points.

obtained. This supports the above rate equation, and gives the following values of k:

Run	1	2	3	4	5	6	7	8	9	10	
k	6.28	6.99	6.94	6.17	5.67	6.07	5.58	6.72	6.40	5.65	$\times 10^{-4}$ min.$^{-1}$

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Before accepting these values of the constants, we must correct them for the effect of the decomposition of hypochlorite to chlorate, and for the effect of the secondary reaction. If the total reaction followed the second equation to nitrate and carbonate, the rate equations would be:

$$-dx/dt = 4kxy/z, \qquad dx/dt = 4\,dy/dt = 2\,dz/dt.$$

These give on integration:

$$[\text{ii}] \qquad -kt = \frac{1}{x_0-4y_0}\left[(\tfrac{1}{2}x_0-z_0)\ln\frac{x}{x_0}+(z_0-2y_0)\ln\frac{(x-x_0+4y_0)}{4y_0}\right].$$

This equation gives a curve only a little different from equation [i], if we take the best value of k to fit the experimental points. In runs 2 and 3 where the secondary reaction is the most important, equation [ii] gives a curve which deviates from the experimental points in the opposite direction from equation [i], so a combination of both gives an excellent fit.

In a more general way, if c is the chance that the second reaction will occur (i.e. $c = b/a$), and $(1-c)$ is the chance that the first reaction will occur; then $(3+c)$ hypochlorite ions, $(2-c)$ cyanate ions, and 2 hydroxide ions will be used up for each initial step. This leads to the more general equation:

$$[\text{iii}] \quad -kt = \frac{1}{(3+c)\,y_0-(2-c)\,x_0}\left[\left(z_0-\frac{2x_0}{3+c}\right)\ln\frac{x}{x_0} + \left(\frac{2y_0}{2-c}-z_0\right)\ln\frac{(3+c)\,y_0}{(3+c)\,y_0+(2-c)(x-x_0)}\right].$$

If $c = 0$ this reduces to equation [i], and if $c = 1$ it reduces to equation [ii]. It is assumed that reaction II has the same initial step as reaction I. The evidence for this is not very definite because reaction II is masked by the predominant reaction I. However it will be shown in the calculations which follow that in the runs (runs 2 and 3) when the second reaction is most important, the rate constant of reaction I is still in reasonable agreement with that found in other runs; nor is there any apparent relation between this rate constant and b/a. Also, in various runs values of b run roughly parallel to those for a, measured at the same time. For these reasons, and in the absence of definite evidence to the contrary, it seemed simplest to suppose that the two reactions had the same initial step.

Calculating k from equation [iii], we get:

Run	1	2	3	4	5	6	7	8	9	10	
k	5.94	5.27	5.58	5.90	5.67	5.53	5.17	6.04	6.14	5.27	$\times 10^{-4}$ min.$^{-1}$

The reaction to chlorate can be corrected for as follows. The amount of hypochlorite reacting in this way was calculated earlier in obtaining the b/a ratios. This was between $\frac{1}{2}$ and $8\frac{1}{2}\%$ of the total hypochlorite reacting; and it was assumed that the rate constants (which are proportional to the rate of disappearance of hypochlorite) would be too high by the same per cent, as obtained above from equation [iii]. As a result the corrected values were:

Run	1	2	3	4	5	6	7	8	9	10	
% corrn.	1.47	3.98	6.79	0.65	0.53	8.37	1.63	3.51	6.82	1.29	
k(corr.)	5.85	5.06	5.20	5.86	5.64	5.07	5.09	5.83	5.72	5.20	$\times 10^{-4}$ min.$^{-1}$

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The mean value of k was 5.45×10^{-4}, with an average deviation of 0.33×10^{-4}. These values of k can be described as only moderately constant, but it is believed that this is due to the experimental errors in the analyses, and not to the selection of the wrong kinetic scheme. It will be noted that run 7, when a considerable quantity of sodium carbonate was added, gave the same constant, so presumably sodium carbonate and chloride do not catalyze the reaction, apart from their effect on the ionic strength.

We can apply similar calculations to the results in Tables II and III. The data that determine the relative extent of the two reactions are given in Table VIII. The values of b/a in Table VIII show much the same trends as

TABLE VIII

Run	Ionic strength	Temp., ° C.	Change in (OCl^-)	Change in (OCN^-)	Corrn. to OCl^-	Corrected change in (OCl^-)	a	b	b/a
11	1.7	65	0.2125	0.140	0.005	0.2075	0.0705	(−.001)	0
12	2.0	65	0.123	0.066	0.008	0.115	0.0298	0.0064	0.21
13	2.9	65	0.306	0.126	0.046	0.260	0.0488	0.0284	0.58
14	3.5	65	0.0995	0.054	0.0015	0.098	0.0236	0.0068	0.28
15	2.2	55	0.0775	0.036	0.002	0.0755	0.0185	0.0050	0.27
16	2.2	75	0.193	0.0945	0.003	0.0190	0.0398	0.0184	0.46
17	2.2	50	0.2355	0.128	0.0135	0.222	0.0580	0.0136	0.23

before. In run 13, for instance, the high hypochlorite concentration makes b/a high. The run at 75° C. seems to have a high value of b/a, and it is of course reasonable to suppose that temperature could alter the extent of these reactions. The numbers do give some indication that high temperature or ionic strength both increase b/a, but the results are too few for any firm conclusions to be drawn.

If we evaluate k precisely as before, the final corrected results are:

Run	11	12	13	14	15	16	17	
Temp.	65	65	65	65	55	75	50	° C.
Ionic strength	1.7	2.0	2.9	3.5	2.2	2.2	2.2	
k	4.22	4.85	5.52	6.20	1.89	16.8	1.00	$\times 10^{-4}$ min.$^{-1}$

The results for run 13 cannot be very accurate because of the large correction for the reaction to chlorate. The values of k show an upward drift with ionic strength; the extent of the change is comparable with that found in similar reactions, e.g. that of hypochlorite going to chlorate.

If log k is plotted against $1/T$ in the usual way, a fairly straight line is obtained. The over-all (50° C. to 75° C.) value for the activation energy is 25.3 kcal./gm-mol. If we allow a little more weight to the value at 65° C., because it was more carefully measured, the activation energy is reduced a little: probably the best value is $25(\pm\frac{1}{2})$ kcal./gm-mol.

Comparison of the observed and calculated gas rates for runs 11 to 17 as given in Table VII(b) shows about the same degree of agreement as before. The calculated rates were obtained in the same way as in Table VII(a).

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The next question is that of what one can conclude about the mechanism of this reaction. The kinetics suggest that the slow step is really a bimolecular reaction of HOCl and OCN^-. If k_t is the true rate constant of this reaction, then comparison with the rate equations used earlier shows that:

$$k_t(HOCl) = k(OCl^-)/(OH^-)$$

[iv] or $$k_t = K_a.k/K_w$$

where K_a is the ionization constant of hypochlorous acid, and K_w is the ionization constant of water. At 65° C., k is 5.45×10^{-4} and K_w is 1.25×10^{-13} (2). There are no values of K_a reported for 65° C., but it is 3.8×10^{-8} at 27° C. (5). If we use the value of the heat of ionization given below, the calculated ionization constant at 65° C. is 8×10^{-8}. Hence k_t at 65° C. is 350 min.$^{-1}$ M.p.l.$^{-1}$, or 5.8 sec.$^{-1}$ M.p.l^{-1}. This is a fairly fast reaction, and the question arises whether this is consistent with the observed temperature dependence on the rate. By taking $-1/R \cdot d \ln/d(1/T)$ of both sides of equation [iv] we get:

$$E_t = E + q_a - q_w$$

where E_t is the true activation energy of the reaction of HOCl with OCN^-, and E is the apparent activation energy (25 kcal.) obtained above. q_a is the heat of the reaction:

$$H^+ + OCl^- \rightarrow HOCl + q_a$$

and q_w is the heat of recombination of the ions of water: 13.8 kcal. (1). There seem to be no direct values for the heat of ionization of hypochlorous acid, but data given by Latimer (3) make q_a = 3.9 kcal. Substituting these values, E_t = 15.1 kcal./gm-mol. This cannot be considered to be very accurate, chiefly because of uncertainty in q_a. If, as is usual, we suppose that k_t and E_t are related by $k_t = Ae^{-E_t/RT}$, then the value of log A is 10.5. This is quite a plausible value for A; and, while no great accuracy can be claimed, it seems safe to conclude that there is no inconsistency in the observed rates and temperature dependence.

Finally, if the first step is a reaction of hypochlorous acid and cyanate ions, it is natural to consider what might be the intermediate products of such a reaction. Unfortunately these products are not obvious, and what follows is largely speculation. However it is perhaps reasonable to assume that chloride ions are formed, as in other oxidations by hypochlorous acid. The reaction might then be:

$$HOCl + OCN^- + H_2O \rightarrow Cl^- + HO_2CNHOH$$

followed by further rapid oxidation. Alternatively, HOCl might possibly add across a double or triple bond in a cyanate ion, to give the rather awkward looking ion $(O{=}C.OH{-}NCl)^-$ which would doubtless rearrange to $(O_2C{-}NHCl)^-$. The first suggestion looks rather more plausible. At least one can conclude that such products are not wholly ridiculous, and the kinetics presumably show that some such reaction really occurs.

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ÉTUDES SUR LA SYNTHÈSE DE L'HYDROXYPROLINE À PARTIR DE DÉRIVÉS DE L'ACIDE 2-AMINO-4-PENTÈNOÏQUE[1]

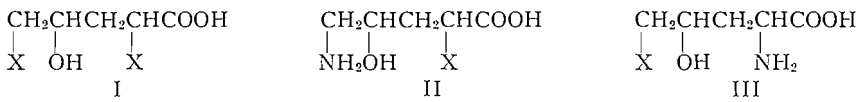
PAR ROGER GAUDRY, LOUIS BERLINGUET, ANDRÉ LANGIS ET GÉRARD PARIS

ABSTRACT

A systematic investigation of the synthesis of 4-hydroxy-DL-proline and 2-amino-4-dihydroxyvaleric acid has been made, starting from the following derivatives of 2-amino-4-pentenoic acid: ethyl allylacetamidomalonate, ethyl allylacetamidocyanoacetate, 2-phthalimidopentenoic acid, allylacetamidomalonic acid, acetylallylglycine, 5-allylhydantoin, and 3-phenyl-5-allylhydantoin. Chlorine or bromine was added to the double bond of these compounds, and the reaction products were either derivatives of 5-halogenated-4-valerolactones or derivatives of 4,5-dihalogenated pentanoic acids, depending on whether the carboxyl group of the pentanoic acid was free or not when the halogenation reaction was carried out. Acid hydrolysis followed by treatment with barium hydroxide always gave mixtures, in different ratio, of 4-hydroxy-DL-proline and 2-amino-4,5-dihydroxyvaleric acid which were analyzed and isolated as the copper salts. In the case of 5-(2,3-dibromopropyl)hydantoin and 3-phenyl-5-(2,3-dibromopropyl)hydantoin, no cyclization could be obtained.

INTRODUCTION

Nous avons entrepris d'étudier systématiquement la synthèse de la 4-hydroxyproline dans le but d'élaborer une synthèse permettant l'obtention facile de grandes quantités de cet acide aminé naturel. On peut ramener à trois méthodes générales les synthèses de l'hydroxyproline publiées à date. La première consiste à cycliser par l'ammoniac un dérivé 2,5-dihalogéné de l'acide 4-hydroxyvalérianique (I), donc un produit ne contenant pas d'azote. La deuxième consiste à cycliser par une base un dérivé 2-halogéné de l'acide 4-hydroxy-5-aminovalérianique (II), c'est-à-dire une substance renfermant de l'azote aminé en position 5. La troisième consiste au contraire à cycliser par une base un dérivé 5-halogéné de l'acide 2-amino-4-hydroxyvalérianique (III), renfermant par conséquent de l'azote aminé en position 2.



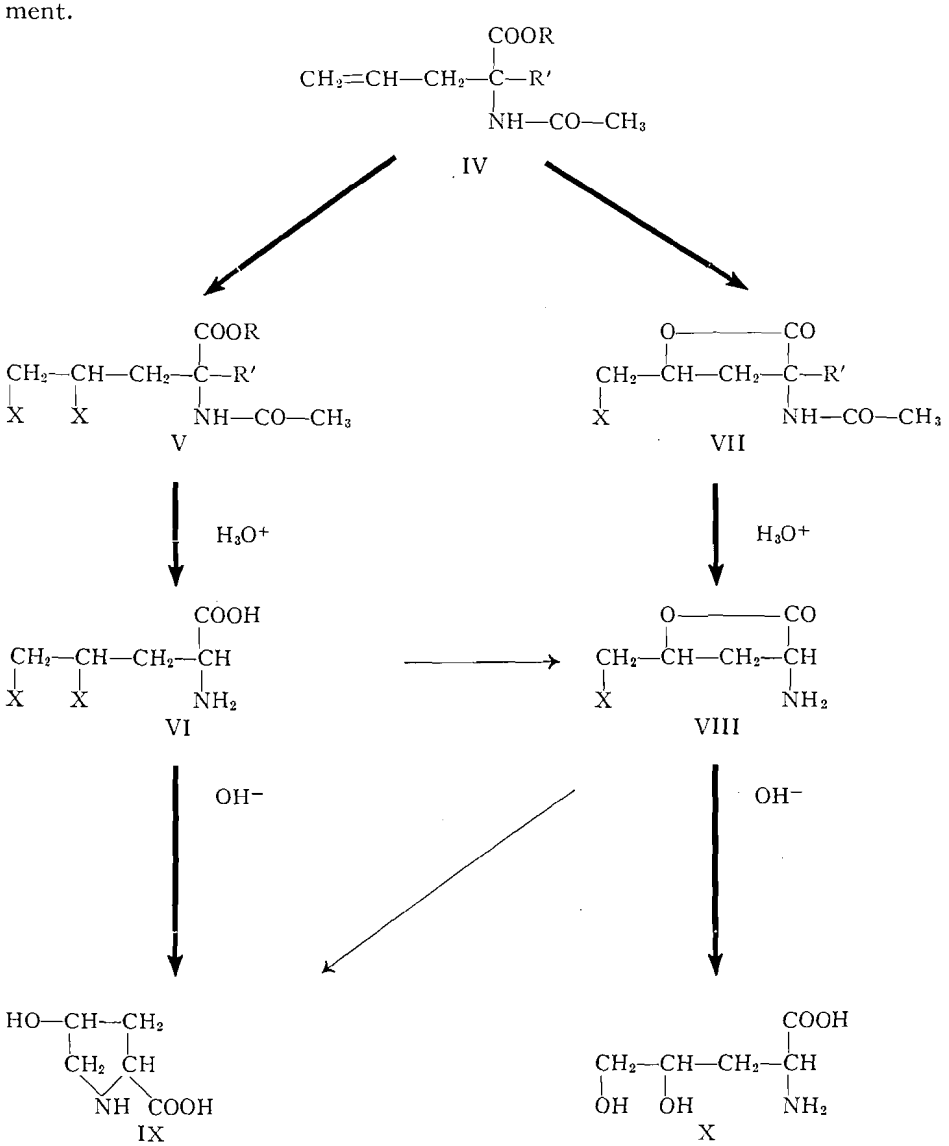
Dans une publication antérieure (5), nous avons discuté de la synthèse de l'hydroxyproline à partir de dérivés 2,5-dihalogénés de l'acide 4-hydroxyvalérianique (I) et 2-halogénés de l'acide 4-hydroxy-5-aminovalérianique (II). Nous exposons maintenant les résultats de nos travaux sur la préparation de l'hydroxyproline en passant par les dérivés 5-halogénés de l'acide 2-amino-4-hydroxyvalérianique (III).

On trouve dans la littérature quatre synthèses de l'hydroxyproline qui utilisent l'acide 2-amino-4-hydroxy-5-halogénovalérianique comme intermédiaire: celle de Fischer et Krämer (3), Hammarsten (6), McIlwain et Richardson (9) ainsi que Feofilaktov et Onishchenko (2). Mais celle de Hammarsten est la seule à utiliser comme produit de départ un dérivé de l'acide 2-amino-4-pentènoïque: l'acide allylhippurique ou acide 2-benzamido-4-pentènoïque.

[1]*Manuscrit reçu pour la première fois le 18 août 1955, et sous forme revisée le 29 décembre 1955.*
Contribution du Département de Biochimie de la Faculté de Médecine, Université Laval, Québec, P.Q.

Nous avons repris la méthode de Hammarsten, et nous l'avons appliquée, avec modifications appropriées, à plusieurs types de dérivés de l'acide 2-amino-4-pentènoïque, soit: l'allylacétamidomalonate d'éthyle (IV, $R=C_2H_5$, $R'=CO_2C_2H_5$), l'allylacétamidocyanoacétate d'éthyle (IV, $R=C_2H_5$, $R'=CN$), l'acide 2-phtalimido-4-pentènoïque (IV, $R=R'=H$, $-N(CO)_2C_6H_4$ remplace $-NHCOCH_3$), l'acide allylacétamidomalonique (IV, $R=H$, $R'=COOH$), l'acétylallylglycine (IV, $R=R'=H$), la 5-allylhydantoïne ainsi que la 3-phényl-5-allylhydantoïne.

Par addition de chlore ou de brome à l'allylacétamidomalonate d'éthyle (IV, $R=C_2H_5$, $R'=CO_2C_2H_5$), on obtient les esters correspondants à l'état cristallin: le dichloré avec 18% de rendement; le dibromé avec 50% de rendement.



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Par addition de chlore ou de brome à l'allylacétamidocyanoacétate d'éthyle (IV, $R = C_2H_5$, $R' = CN$), on obtient les esters correspondants à l'état cristallin mais qui sont beaucoup plus faciles à cristalliser et à isoler que les produits analogues provenant de l'allylacétamidomalonate d'éthyle (IV, $R = C_2H_5$, $R' = CO_2C_2H_5$). L'ester dichloré est obtenu avec un rendement de 70% et l'ester dibromé avec un rendement de 75%.

L'addition d'halogènes sur l'acide 2-phtalimido-4-pentènoïque (IV, $R = R' = H$, $—N(CO)_2C_6H_4$ remplace $—NHCOCH_3$), sur l'acide allylacétamidomalonique (IV, $R = H$, $R' = COOH$) et sur l'acétylallylglycine (IV, $R = R' = H$) donne surtout les dérivés de la 2-amino-4-valérolactone-5-halogénée, les acides dihalogénés se cyclisant avec le groupement carboxyle libre.

L'hydrolyse acide des dérivés 4,5-dihalogénés donne surtout l'acide 2-aminovalérianique-4,5-dihalogéné. Et par chauffage en milieu alcalin, on obtient la 4-hydroxyproline (IX) avec de l'acide 2-amino-4,5-dihydroxyvalérianique (X) comme sous-produit.

Par contre, l'hydrolyse acide des dérivés de la 2-amino-4-valérolactone-5-halogénée (VII), suivie de chauffage en milieu alcalin, mène de préférence à l'acide 2-amino-4,5-dihydroxyvalérianique (X), avec la 4-hydroxyproline (IX) comme produit secondaire. On peut expliquer ces résultats en considérant que, par traitement alcalin, l'anneau des lactones doit s'ouvrir avant que l'anneau de pyrrolidine puisse se former. Il y a alors réactions compétitives entre l'hydrolyse de la lactone et le remplacement de l'atome d'halogène en position 5 par une fonction alcool. Lorsque l'atome d'halogène est un atome de brome, il semble que dans la majorité des cas, il soit en bonne partie éliminé avant l'ouverture de l'anneau de l'acide 2-amino-4,5-dihydroxyvalérianique. Lorsque l'atome d'halogène est l'atome de chlore, il réagit lentement avec l'alcali. Dans ce cas, il peut se former une quantité appréciable d'acide 2-amino-4-hydroxy-5-chlorovalérianique qui se cyclise aussitôt en hydroxyproline.

En conséquence, les lactones bromées mènent presque exclusivement à l'acide dihydroxylé tandis que les lactones chlorées mènent à des mélanges d'hydroxyproline et d'acide dihydroxylé.

Les essais de séparation de ces deux acides aminés au moyen des picrates (7), des sels de reineke (10), des chlorhydrates, ainsi que la séparation sur des colonnes de résines se sont avérés infructueux.

Nous avons réussi à effectuer la séparation des deux acides aminés par cristallisation fractionnée des sels de cuivre de l'hydroxyproline et de l'acide dihydroxylé dans l'eau puis dans l'alcool méthylique anhydre. Ainsi nous avons pu isoler le sel de cuivre de l'acide dihydroxylé, qui jusqu'alors n'avait jamais été isolé de façon certaine (3,6) et le sel de cuivre de l'hydroxyproline. Nous n'avons toutefois pas tenté la séparation des formes "allo" et "DL".

Quant à l'étude des meilleures conditions expérimentales pour ces synthèses, nous avons déterminé les rendements des deux acides aminés, hydroxyproline et acide 2-amino-4,5-dihydroxyvalérianique, par dosage chimique au moyen respectivement des méthodes de McFarlane et Guest (8) et de N. W. Rees (11). Cette dernière méthode avait été tout d'abord employée pour doser la sérine

et la thréonine. Nous l'avons adoptée au dosage de l'acide 4,5-dihydroxylé avec tout autant de succès.

Ces analyses ont été effectuées sur les liqueurs provenant de l'hydrolyse acide et du traitement alcalin des produits dihalogénés (Tableau I). Elles ont aussi été déterminées sur les solutions obtenues après halogénation, hydrolyse acide, traitement alcalin des dérivés de l'acide 2-amino-4-pentènoïque (Tableau II). Les différences entre les valeurs des deux tableaux, proviennent évidemment des difficultés rencontrées lors de l'isolement des produits intermédiaires.

TABLEAU I

RENDEMENTS EN HYDROXYPROLINE ET EN ACIDE 2-AMINO-4,5-DIHYDROXYVALÉRIANIQUE PAR ANALYSE DE LA SOLUTION APRÈS HYDROLYSE ACIDE ET CYCLISATION ALCALINE DU PRODUIT DIHALOGÉNÉ ISOLÉ

	Rendement en %		
	Hydroxyproline	Acide dihydroxylé	Total
Ester éthylique de l'acide 2-carbéthoxy-2-acétamido-4,5-dichlorovalérianique	69	13	82
Ester éthylique de l'acide 2-carbéthoxy-2-acétamido-4,5-dibromovalérianique	57	33	90
Ester éthylique de l'acide 2-acétamido-2-cyano-4,5-dichlorovalérianique	79	17	96
Ester éthylique de l'acide 2-acétamido-2-cyano-4,5-dibromovalérianique, p.f. 131° C.	25	63	88
2-Phtalimido-5 chlorovalérolactone	27	38	65
2-Phtalimido-5-bromovalérolactone	7	65	72

TABLEAU II

RENDEMENTS EN HYDROXYPROLINE ET EN ACIDE 2-AMINO-4,5-DIHYDROXYVALÉRIANIQUE PAR ANALYSE DE LA SOLUTION APRÈS HALOGÉNATION, HYDROLYSE ACIDE ET CYCLISATION ALCALINE DES DÉRIVÉS DE L'ACIDE 2-AMINO-4-PENTÈNOÏQUE

		Rendement en %		
		Hydroxyproline	Acide dihydroxylé	Total
Allylacétamidomalonate d'éthyle plus:	Cl_2 à 0° C.	74	13	87
	Cl_2 à 25° C.	67	23	90
	SO_2Cl_2 à 25° C.	78	17	95
	Br_2 à 0° C.	13	51	64
	Br_2 à 25° C.	28	49	77
Allylacétamidocyanoacétate d'éthyle plus:	Cl_2 à 25° C.	52	18	70
	SO_2Cl_2 à 25° C.	64	24	88
	Br_2 à 25° C.	48	37	85
Acide 2-phtalimido-4-pentènoïque plus:	Cl_2 à 25° C.	21	57	78
	Br_2 à 25° C.	24	48	72

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Dans une publication récente portant sur la proline, l'un de nous (4) a démontré qu'on peut cycliser la 5-(3-chloropropyl)hydantoïne en l'hydantoïne de la proline, et que la 3-phenyl-5-(3-bromopropyl)hydantoïne se cyclise spontanément en phénylhydantoïne de la proline. Nous avons voulu appliquer ces réactions à l'hydroxyproline. Nous avons préparé la 5-(2,3-dibromopropyl) hydantoïne, ainsi que la 3-phenyl-5-(2,3-dibromopropyl)hydantoïne. Mais tous nos essais de cyclisation de ces hydantoïnes en dérivés de l'hydroxyproline se sont avérés infructueux.

Il ressort de ces travaux que la préparation des acides 2-aminovalérianique-4,5-dihalogénés, conduisant à l'hydroxyproline ne peut se faire sans qu'une certaine partie de l'acide ne se cyclise en 2-amino-4-valérolactone-5-halogénée, laquelle lactone, par traitement alcalin, donne surtout l'acide 2-amino-4,5-dihydroxyvalérianique. Les quantités d'hydroxyproline obtenues, quoique élevées, sont toujours accompagnées de l'acide 2-amino-4,5-dihydroxyvalérianique qu'on peut fort heureusement séparer par la méthode décrite plus haut.

PARTIE EXPÉRIMENTALE

Allylacétamidomalonate d'éthyle (*IV*, $R = C_2H_5$, $R' = CO_2C_2H_5$)

Dans un ballon à 3 cols de 300 ml. muni d'un agitateur, d'un réfrigérant surmonté d'un tube de chlorure de calcium et d'un entonnoir à décantation, on place 100 ml. d'alcool anhydre dans lequel on dissout du sodium (4.6 g., 0.20 mole). On ajoute ensuite de l'acétamidomalonate d'éthyle (43.4 g., 0.20 mole). Après environ une demi-heure, on laisse tomber goutte à goutte du bromure d'allyle (28 g., 0.23 mole) en maintenant la température à 25° C. L'addition terminée on chauffe la solution à 40° C. pendant 20 h. L'alcool est évaporé sous pression réduite, puis on dissout le résidu dans 10 ml. d'eau distillée. Après avoir acidifié la solution avec de l'acide sulfurique, on extrait l'allylacétamidomalonate d'éthyle à l'éther. On sèche la solution éthérée sur du sulfate de sodium anhydre. L'éther est ensuite évaporé sous pression réduite et le produit de condensation cristallise lentement. On le recristallise de l'alcool éthylique aqueux. Rendement: 37 g., 72%. P. f.* 46° C., Litt.: 46° C. (1). Calculé pour $C_{12}H_{19}O_5N$: N, 5.45%. Trouvé: N, 5.41%.

Lorsqu'on substitue le chlorure d'allyle au bromure d'allyle, le rendement est de 45%.

Ester éthylique de l'acide 2-carbéthoxy-2-acétamido-4,5-dichlorovalérianique (*V*, $X = Cl$, $R = C_2H_5$, $R' = CO_2C_2H_5$)

Dans un ballon à large col de 300 ml., on dissout de l'allylacétamidomalonate d'éthyle (9 g., 0.035 mole) dans 50 ml. de chloroforme. On refroidit la solution à 10° C. et on y fait barbotter du chlore jusqu'à addition du poids théorique. On évapore le solvant sous pression réduite et on dissout le résidu gommeux obtenu dans 25 ml. d'alcool éthylique. On verse la solution alcoolique dans de l'eau glacée. Le produit dichloré cristallise. Après recristallisation de l'alcool dilué le rendement est de: 2 g., 18%. P. f. 54–61° C. Calculé pour $C_{12}H_{19}O_5NCl_2$: N, 4.28%; Cl, 21.4%. Trouvé: N, 4.25%; Cl, 22.2%. On peut aussi faire l'addition de chlore au moyen de chlorure de sulfuryle.

**Les points de fusion ne sont pas corrigés.*

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Ester éthylique de l'acide 2-carbéthoxy-2-acétamido-4,5-dibromovalérianique (V, $X = Br$, $R = C_2H_5$, $R' = CO_2C_2H_5$)

On place de l'allylacétamidomalonate d'éthyle (20 g., 0.078 mole) et 50 ml. de chloroforme dans un ballon à large col de 500 ml. Après dissolution, on ajoute goutte à goutte du brome (15 g., 0.094 mole) dissous dans 10 ml. de chloroforme, en maintenant la température à 20° C. Le solvant est ensuite évaporé. On se débarrasse de l'excès de brome en utilisant une solution aqueuse de bisulfite de sodium. On dissout le résidu gommeux dans 25 ml. d'alcool éthylique et on verse la solution dans de l'eau glacée. Le produit dibromé cristallise. On le recristallise de l'alcool dilué. Rendement: 17 g., 50%. P. f. 85° C. Calculé pour $C_{12}H_{19}O_5NBr_2$: N, 3.35%; Br, 38.3%. Trouvé: N, 3.47%; Br, 39.3%.

Hydrolyse et cyclisation alcaline

(*a*) *A partir de l'ester éthylique de l'acide 2-carbéthoxy-2-acétamido-4,5-dichlorovalérianique*

L'ester éthylique de l'acide 2-carbéthoxy-2-acétamido-4,5-dichlorovalérianique (1 g., 0.0031 mole) est dissous dans 15 ml. d'acide acétique glacial, puis hydrolysé par 25 ml. d'acide chlorhydrique concentré pendant quatre heures. On évapore la solution à sec sous pression réduite et on reprend le résidu à l'eau. On ajoute un excès d'hydroxyde de baryum (0.8 g., 0.0047 mole) et l'on chauffe à reflux pendant 16 h. L'hydroxyde de baryum est précipité avec du carbonate d'ammonium. Après avoir filtré le carbonate de baryum, la solution est évaporée à sec sous pression réduite. Le résidu est repris à l'eau, traité au noir animal, filtré et analysé par la méthode de McFarlane and Guest (8) pour l'hydroxyproline et la méthode de M. W. Rees (11) pour l'acide 2-amino-4,5-dihydroxyvalérianique. Le dosage de la solution donne les rendements suivants: hydroxyproline, 69%; acide 2-amino-4,5-dihydroxyvalérianique, 13%.

Lorsque l'on additionne à 25° C. du chlorure de sulfuryle (2.7 g., 0.020 mole) à l'allylacétamidomalonate d'éthyle (5 g., 0.019 mole) sans isoler le produit dichloré, l'on obtient, après hydrolyse et cyclisation alcaline, les rendements suivants calculés par analyse à partir de l'allylacétamidomalonate d'éthyle: hydroxyproline, 78%; acide 2-amino-4,5-dihydroxyvalérianique, 17%.

(*b*) *A partir de l'ester éthylique de l'acide 2-carbéthoxy-2-acétamido-4,5-dibromovalérianique*

En procédant de la même façon l'ester éthylique de l'acide 2-carbéthoxy-2-acétamido-4,5-dibromovalérianique (1 g., 0.0024 mole) donne par hydrolyse et cyclisation alcaline les rendements suivants calculés par analyse: hydroxyproline, 57%; acide 2-amino-4,5-dihydroxyvalérianique, 33%.

Lorsque l'on additionne à 25° C. du brome (3.6 g., 0.0225 mole) à l'allylacétamidomalonate d'éthyle (5 g., 0.0195 mole) sans isoler le produit dibromé, l'on obtient après hydrolyse et cyclisation alcaline les rendements suivants calculés par analyse à partir de l'allylacétamidomalonate d'éthyle: hydroxyproline, 28%; acide 2-amino-4,5-dihydroxyvalérianique, 49%.

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Acétamidocyanoacétate d'éthyle

L'acétamidocyanoacétate d'éthyle a été préparé par la méthode de l'hydrosulfite (12). L'isonitrosocyanoacétate d'éthyle formé par l'action de l'acide nitreux sur le cyanoacétate d'éthyle n'a pas été isolé mais immédiatement réduit par l'hydrosulfite de sodium en présence d'anhydride acétique. Rendement: 51%. P. f. 129° C. Le produit est recristallisé de l'acide acétique 15%.

Allylacétamidocyanoacétate d'éthyle (*IV*, $R = C_2H_5$, $R' = CN$)

On place 75 ml. d'alcool anhydre dans un ballon à 3 cols muni d'un agitateur et d'un réfrigérant surmonté d'un tube de chlorure de calcium. On y dissout du sodium (4.6 g., 0.2 mole), puis on refroidit la solution à 10–15° C. On ajoute de l'acétamidocyanoacétate d'éthyle (34 g., 0.2 mole). Après 15 min. on élève la température à 30–35° C. et on laisse tomber goutte à goutte du chlorure d'allyle (25 g., 0.33 mole). L'addition du chlorure terminée, on élève la température à 60–65° C. et l'on chauffe ainsi la solution pendant huit heures. On verse la solution dans un mélange d'eau et de glace et on obtient des cristaux d'allylacétamidocyanoacétate d'éthyle que l'on filtre et que l'on lave à l'eau froide. Rendement: 39 g., 93%. P. f. 89° C., Litt. 89° C. (1). Calculé pour $C_{10}H_{14}O_3N_2$: N, 13.3%. Trouvé: N, 12.9%. En substituant le bromure d'allyle, le rendement est à peu près le même.

Ester éthylique de l'acide 2-acétamido-2-cyano-4,5-dichlorovalérianique (*V*, $X = Cl$, $R = C_2H_5$, $R' = CN$)

L'addition de chlore gazeux sur l'allylacétamidocyanoacétate d'éthyle (25 g., 0.12 mole) dissous dans le chloroforme à 10° C. suivant la méthode décrite pour l'ester éthylique de l'acide 2-carbéthoxy-2-acétamido-4,5-dichlorovalérianique donne le produit dichloré avec un rendement de: 25 g., 70%. P. f. 100–105° C. Calculé pour $C_{10}H_{14}O_3N_2Cl_2$: N, 10.27%; Cl, 25%. Trouvé: N, 9.80%; Cl, 26.1%.

Ester éthylique de l'acide 2-acétamido-2-cyano-4,5-dibromovalérianique (*V*, $X = Br$, $R = C_2H_5$, $R' = CN$)

De la même façon que pour l'ester éthylique de l'acide 2-carbéthoxy-2-acétamido-4,5-dibromovalérianique, l'addition de brome (16 g., 0.1 mole) à l'allylacétamidocyanoacétate d'éthyle (20 g., 0.095 mole) à 20–25° C. dans le chloroforme donne 26 g. de produit. Rendement: 75%. P. f. 114–115° C. Calculé pour $C_{10}H_{14}O_3N_2Br_2$: N, 7.56%; Br, 43.3%. Trouvé: N, 7.56%; Br, 43.2%.

Le produit isolé contient un mélange des deux isomères possibles. Si l'on fait la bromuration à −5°–0° C. le produit dibromé fond à 131° C. Si par ailleurs la bromuration est effectuée à 40–45° C. l'isomère dibromé obtenu fond à 98–99° C.

5-Bromo-2-acétamido-2-cyano-4-valérolactone (*VII*, $X = Br$, $R' = CN$)

L'ester éthylique de l'acide 2-cyano-2-acétamido-4,5-dibromovalérianique (7.4 g., 0.02 mole) est dissous dans 100 ml. d'alcool absolu bouillant. On ajoute un équivalent de potasse alcoolique (1.12 g., 0.02 mole) puis l'on chauffe le

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mélange à reflux pendant quatre heures. On laisse refroidir et on filtre le précipité de bromure de potassium. On évapore le solvant. On reprend le résidu à l'éther pour enlever les dernières traces de bromure et on filtre. L'éther est évaporé et l'on obtient comme résidu une huile blanche difficile à cristalliser. Poids: 1 g. P. f. 85° C. Calculé pour $C_8H_9O_3N_2Br$: N, 10.7%; Br, 30.6%. Trouvé: N, 10.9%; Br, 30.1%.

Hydrolyse et cyclisation alcaline

(*a*) *A partir de l'ester éthylique de l'acide 2-acétamido-2-cyano-4,5-dichlorovalérianique*

L'ester éthylique de l'acide 2-acétamido-2-cyano-4,5-dichlorovalérianique (2 g., 0.0071 mole) hydrolysé et cyclisé de la même façon que l'ester éthylique de l'acide 2-carbéthoxy-2-acétamido-4,5-dichlorovalérianique donne les rendements suivants obtenus par analyse: hydroxyproline, 79%; acide 2-amino-4,5-dihydroxyvalérianique, 17%.

Lorsque l'on additionne à 25° C. du chlorure de sulfuryle (2 g., 0.015 mole) à l'allylacétamidocyanoacétate d'éthyle (2 g., 0.010 mole) sans isoler le produit dichloré, l'on obtient après hydrolyse et cyclisation alcaline les rendements suivants calculés à partir de l'allylacétamidocyanoacétate d'éthyle et obtenus par analyse: hydroxyproline, 64%; acide 2-amino-4,5-dihydroxyvalérianique, 24%.

(*b*) *A partir de l'ester éthylique de l'acide 2-acétamido-2-cyano-4,5-dibromovalérianique*

L'ester éthylique de l'acide 2-acétamido-2-cyano-4,5-dibromovalérianique (2 g., 0.005 mole), p.f. 131° C., en procédant de la même façon qu'à partir de l'ester éthylique de l'acide 2-carbéthoxy-2-acétamido-4,5-dichlorovalérianique, donne les rendements suivants obtenus par analyse: hydroxyproline, 25%; acide 2-amino-4,5-dihydroxyvalérianique, 63%.

Par addition de brome à 25° C. (2 g., 0.0125 mole) sur l'allylacétamidocyanoacétate d'éthyle (2 g., 0.0095 mole) et sans isoler le produit dibromé, on obtient par analyse, après hydrolyse et cyclisation alcaline, les rendements suivants: hydroxyproline, 48%; acide 2-amino-4,5-dihydroxyvalérianique, 37%.

Allylglycine

Dans un ballon de 300 ml., on place de l'allylacétamidocyanoacétate d'éthyle (10 g., 0.047 mole). On y ajoute 150 ml. d'eau distillée et 10 ml. d'acide sulfurique concentré. Après avoir chauffé la solution à reflux pendant quatre heures, on la neutralise avec de l'hydroxyde de baryum. On filtre le précipité de sulfate de baryum et on se débarrasse de l'excès d'hydroxyde de baryum en le faisant réagir avec un excès de carbonate d'ammonium. On filtre et on évapore la solution à sec sous pression réduite. On reprend le précipité avec 25 ml. d'eau distillée. On décolore la solution au noir animal et on précipite l'acide aminé en ajoutant 75 ml. d'alcool éthylique à la solution aqueuse. On filtre l'allylglycine et on sèche à l'air. Rendement: 2.5 g., 46%. P. f. 246–248° C. Calculé pour $C_5H_9O_2N$: N, 12.16%. Trouvé: N, 12.13%.

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Acide 2-phtalimido-4-pentènoïque (*IV*, $R=R'=H$, $—N(CO)_2C_6H_4$ *remplace* $—NHCOCH_3$)

Dans un ballon de 100 ml., on place un mélange intime d'allylglycine (11.5 g., 0.1 mole) et d'anhydride phtalique (14.8 g., 0.1 mole) que l'on chauffe à une température de 180° C. pendant 10 min. Après avoir refroidi le produit, on le cristallise de l'alcool éthylique aqueux à 40% (125 ml.). Rendement: 21 g., 85%. P. f. 120–121° C. Calculé pour $C_{13}H_{11}O_4N$: N, 5.73%. Trouvé: N, 5.89%.

2-Phtalimido-5-chloro-4-valérolactone (*VI*, $X=Cl$, $R'=H$, $—N(CO)_2C_6H_4$ *remplace* $—NHCOCH_3$)

Dans un ballon à large col de 50 ml., on place de l'acide 2-phtalimido-4-pentènoïque (7.35 g., 0.03 mole) que l'on dissout dans 100 ml. d'acide acétique glacial. On y ajoute goutte à goutte, à la température de la chambre, du chlorure de sulfuryle (5 g., 0.037 mole). Le produit de la réaction cristallise de la solution à mesure qu'il se forme. On le recristallise de l'acétone. Rendement: 1.7 g., 20.5%. P. f. 187–188° C. Calculé pour $C_{13}H_{10}O_4NCl$: N, 5.02%; Cl, 12.71%. Trouvé: N, 5.10%; Cl, 12.68%.

2-Phtalimido-5-bromo-4-valérolactone (*VII*, $X=Br$, $R'=H$, $—N(CO)_2C_6H_4$ *remplace* $—NHCOCH_3$)

On dissout de l'acide phtalimidopentènoïque (24.5 g., 0.1 mole) dans 200 ml. d'acide acétique glacial. On ajoute goutte à goutte du brome (12.6 g., 0.079 mole) dans 50 ml. de tétrachlorure de carbone, en maintenant une bonne agitation. Le produit de la réaction cristallise de la solution à mesure qu'il se forme. On le recristallise d'un peu d'acétone. Rendement: 10.2 g., 31%. P. f. 189–190° C. Calculé pour $C_{13}H_{10}O_4NBr$: N, 4.32%; Br, 24.3%. Trouvé: N, 4.33%; Br, 24.4%.

Hydrolyse et cyclisation alcaline

(*a*) *A partir de la 2-phtalimido-5-chloro-4-valérolactone*

La 2-phtalimido-5-chloro-4-valérolactone (1 g., 0.0035 mole) est dissoute dans un mélange de 20 ml. d'acide acétique glacial et de 20 ml. d'acide chlorhydrique concentré. On chauffe à reflux pendant quatre heures, on évapore à sec, on reprend à l'eau et on filtre l'acide phtalique. On neutralise le filtrat avec de l'hydroxyde de baryum et on ajoute un excès d'hydroxyde de baryum 1.8 g. (0.0105 mole). On chauffe à reflux pendant six heures, on précipite le baryum au moyen d'un excès de carbonate d'ammonium et on filtre le précipité de carbonate de baryum. La solution est évaporée à sec sous pression réduite. Le résidu est repris à l'eau, filtré et analysé. Le dosage de la solution donne les rendements suivants: hydroxyproline, 27%; acide 2-amino-4,5-dihydroxyvalérianique, 38%.

Lorsqu'on additionne du chlorure de sulfuryle (2 g., 0.015 mole) à l'acide 2-phtalimido-4-pentènoïque (3 g., 0.012 mole) sans isoler le produit chloré, l'on obtient par analyse après hydrolyse et cyclisation alcaline les rendements suivants: hydroxyproline, 21%; acide 2-amino-4,5-dihydroxyvalérianique, 57%.

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(*b*) *A partir de la 2-phtalimido-5-bromo-4-valérolactone*

De la même façon, par hydrolyse et cyclisation de la 2-phtalimido-5-bromo-4-valérolactone (1 g., 0.0031 mole), l'analyse donne les rendements suivants: hydroxyproline, 7%; acide 2-amino-4,5-dihydroxyvalérianique, 65%.

L'addition de brome (2 g., 0.012 mole) sur l'acide 2-phtalimido-4-pentènoïque (3 g., 0.012 mole), sans isoler le produit bromé, donne par analyse après hydrolyse et cyclisation alcaline les rendements suivants: hydroxyproline, 24%; acide 2-amino-4,5-dihydroxyvalérianique, 48%.

Acide allylacétamidomalonique (*IV*, $R=H$, $R'=COOH$)

On dissout de l'allylacétamidomalonate d'éthyle (25.7 g., 0.1 mole) dans de l'hydroxyde de sodium (11.2 g., 0.28 mole) solubilisé dans 50 ml. d'eau distillée et 50 ml. d'alcool éthylique. On laisse la solution à la température de la chambre pendant 24 h. en maintenant une bonne agitation. A la solution, on ajoute de la glace ainsi que 200 ml. d'acide chlorhydrique concentré. On évapore l'alcool sous pression réduite en ne chauffant que légèrement. L'acide allylacétamidomalonique cristallise lorsqu'on refroidit la solution. Rendement: 13.2 g., 65%. P. f. 100–103° C. Calculé pour $C_8H_{11}O_5N$: N, 6.96%. Trouvé: N, 7.00%.

Acétylallylglycine (*IV*, $R=R'=H$)

Dans un ballon de 300 ml., on place de l'acide allylacétamidomalonique (37 g., 0.185 mole) que l'on chauffe sur un bain de cire à une température de 125° C. jusqu'à ce que le dégagement de CO_2 cesse. Le produit est dissous dans 150 ml. d'eau distillée. On décolore la solution au noir animal et on évapore le solvant sous pression réduite. On dissout le résidu dans du chloroforme et on précipite l'acétylallylglycine avec de l'éther de pétrole. Rendement: 16.5 g., 57.0%. P. f. 112° C. Calculé pour $C_7H_{11}O_3N$: N, 8.92%. Trouvé: N, 8.97%.

Bromuration, hydrolyse et cyclisation alcaline

On dissout de l'acétylallylglycine (8.5 g., 0.054 mole) dans 100 ml. d'acide acétique glacial. A la température de la chambre, on ajoute goutte à goutte du brome (9 g., 0.057 mole) dissous dans 25 ml. de chloroforme en maintenant une bonne agitation. L'addition de brome terminée, on évapore le solvant sous pression réduite et on obtient un résidu gommeux qui se refuse à cristalliser. On y ajoute 150 ml. d'eau distillée et 10 ml. d'acide sulfurique concentré. Après une hydrolyse de quatre heures, on cyclise en milieu alcalin tel que déjà décrit.

La chromatographie sur papier et l'analyse des acides aminés libres montrent que ces sels sont un mélange en parties à peu près égales d'hydroxyproline et d'acide 2-amino-4,5-dihydroxyvalérianique.

On obtient le même résultat à partir de l'acide allylacétamidomalonique au lieu de l'acétylallylglycine.

Formation des sels de cuivre de l'hydroxyproline et de l'acide 2-amino-4,5-dihydroxyvalérianique

Après avoir fait l'hydrolyse acide et la cyclisation alcaline des dérivés dihalogénés ou des lactones halogénées, on précipite les ions halogénés par le carbonate d'argent. Les bromures ou chlorures d'argent sont filtrés et le filtrat

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est saturé d'hydrogène sulfuré. Après filtration, on évapore la solution à sec. Le résidu est dissous dans un minimum d'eau. On prépare les sels de cuivre des acides aminés par ébullition de la solution ainsi obtenue, en présence d'un excès de carbonate cuivrique et on évapore la solution à sec sous pression réduite. On cristallise les sels de cuivre par dissolution dans un petit volume d'eau chaude et addition d'alcool éthylique. Si après quelques heures au froid rien ne précipite, on évapore un peu d'alcool.

Suivant les produits de départ utilisés, les rendements en mélange des sels de cuivre de l'acide dihydroxylé et de l'hydroxyproline varient entre 40 et 60%. Le pourcentage respectif de l'un et de l'autre des acides aminés dans ces mélanges varie suivant les produits de départ (voir les tableaux I et II).

Séparation des sels de cuivre de l'hydroxyproline et de l'acide dihydroxylé

Hydroxyprolinate de cuivre

On sèche à 110° C. un mélange de sels de cuivre (8.5 g.) des deux acides aminés obtenus suivant la méthode décrite plus haut. On reprend par un minimum d'eau à chaud et on porte au froid. Le sel de cuivre, couleur violet, de l'hydroxyproline est insoluble. On le filtre. Poids obtenu: 3.5 g. Calculé pour $C_{10}H_{16}O_6N_2Cu.\frac{1}{2}H_2O$: N, 8.42%. Trouvé: N, 8.40%.

Une partie du sel de cuivre est solubilisée dans l'eau, acidifiée par l'acide acétique, puis saturée par l'hydrogène sulfuré pour précipiter le cuivre. Après filtration, la solution est décolorée au noir animal puis évaporée à sec. On reprend le résidu à l'eau et on fait un chromatogramme. L'hydroxyproline fut identifiée par chromatographie ascendante avec le phénol comme solvant. Seule la tache jaune caractéristique de l'hydroxyproline apparaissait après révélation à la ninhydrine. R_f 0.66. La méthode employée pour isoler l'acide aminé sous forme cristalline fut celle décrite par Gaudry et Godin (5).

2-Amino-4,5-dihydroxyvalérianate de cuivre

Le filtrat, obtenu lors de la filtration de l'hydroxyprolinate de cuivre, est concentré à très faible volume. On ajoute un grand excès d'alcool éthylique et on porte au froid. Un sel de cuivre bleu très pâle précipite. Poids obtenu: 4.4 g. Par ébullition du sel de cuivre dans l'alcool méthylique absolu, on solubilise les dernières traces d'hydroxyprolinate de cuivre. Après avoir filtré, on sèche le sel de cuivre de l'acide 4,5-dihydroxyvalérianique. P. f. 200–205° C. (déc.). Calculé pour $C_{10}H_{20}O_8N_2Cu$: N, 7.78%. Trouvé: N, 7.70%.

La chromatographie révèle la présence d'une seule tache violette, soit l'acide 2-amino-4,5-dihydroxyvalérianique. R_f 0.42.

Le fractionnement des sels de cuivre par la méthode décrite plus haut donne un rendement excellent. Ainsi en partant d'un mélange de 8.5 g. on sépare 3.5 g. d'hydroxyprolinate de cuivre et 4.4 g. de 4,5-dihydroxyvalérianate de cuivre, soit un rendement total de 93%.

Chlorhydrate de la 2-amino-5-hydroxyvalérolactone

L'acide dihydroxylé sous forme libre, obtenu à partir du 2-amino-4,5-dihydroxyvalérianate de cuivre (1 g.), suivant la méthode décrite précédemment, donne une huile visqueuse qu'il est impossible de cristalliser. On reprend à l'alcool éthylique absolu et on fait barbotter de l'acide chlorhydrique gazeux

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jusqu'à ce que le tout se soit solubilisé. A ce stage, on évapore à sec. Le résidu cristallin est repris par un minimum d'alcool anhydre et filtré. Poids du chlorhydrate de la lactone obtenue: 0.4 g. Rendement 43%. P. f. 203–205° C. Calculé pour $C_5H_{10}O_3NCl$: N, 8.36%; Cl, 21.1%. Trouvé: N, 8.40%; Cl, 20.7%.

Acide 2-phényluréido-4-pentènoïque

On dissout de l'allylglycine (1.8 g., 0.015 mole) dans une solution de 0.62 g. d'hydroxyde de soude dans 50 ml. d'eau distillée. A la température de la chambre, on ajoute à la solution de l'isocyanate de phényle (1.9 g., 0.015 mole) en agitant pendant 15 min. On acidifie la solution avec 1.5 ml. d'acide chlorhydrique concentré et on refroidit ensuite sur un bain de glace. On agite le précipité au froid pendant quelques minutes et on filtre le produit. Rendement: 3 g., 85.0%. P. f. 162–163° C. Calculé pour $C_{12}H_{14}O_3N_2$: N, 11.9%. Trouvé: N, 12.1%.

5-Allylhydantoïne

On dissout de l'allylglycine (8.6 g., 0.075 mole) dans 75 ml. d'eau distillée. On ajoute du cyanate de potassium (6.5 g., 0.08 mole) et on chauffe à une température de 65° C. pendant deux heures. On ajoute ensuite à la solution 17.5 ml. d'acide chlorhydrique concentré et on chauffe à 90° C. pendant deux heures. La solution est évaporée à sec sous pression réduite et le résidu est agité dans de l'acétone chaude. Le chlorure de potassium insoluble est filtré et l'acétone est évaporée à sec sous pression réduite. On reprend le résidu avec 100 ml. d'eau bouillante et on décolore la solution au noir animal. On évapore la solution à petit volume, 25 ml. environ, et on place le tout au froid. L'hydantoïne cristallise rapidement. Rendement: 7.4 g., 72%. P. f. 104° C. Calculé pour $C_6H_8O_2N_2$: N, 20.0%. Trouvé: N, 19.5%.

5-(2,3-Dichloropropyl)hydantoïne

On place de la 5-allylhydantoïne (5 g., 0.035 mole) dans 100 ml. de chloroforme. On fait barbotter du chlore gazeux dans la solution jusqu'à saturation, en maintenant cette dernière à la température de la chambre. On évapore à sec sous pression réduite en ne chauffant que légèrement. On recristallise le résidu d'un petit volume d'eau bouillante. Rendement: 3.55 g., 48.5%. P. f. 150–152° C. Calculé pour $C_6H_8O_2N_2Cl_2$: N, 13.25%; Cl, 33.3%. Trouvé: N, 13.20%; Cl, 33.2%.

5-(2,3-Dibromopropyl)hydantoïne

Dans un ballon à large col de 300 ml., on place de l'allylhydantoïne (8.55 g., 0.061 mole) dans 100 ml. de chloroforme. On ajoute goutte à goutte du brome (10.0 g., 0.062 mole) en maintenant la solution à la température de la chambre. On évapore la solution à sec sous pression réduite en ne chauffant que légèrement. On recristallise le résidu d'un volume minimum d'eau bouillante. Rendement: 17 g., 93%. P. f. 155° C. Calculé pour $C_6H_8O_2N_2Br_2$: N, 9.3%; Br, 53.0%. Trouvé: N, 9.3%; Br, 51.1%.

3-Phényl-5-allylhydantoïne

On dissout de l'allylglycine (3.5 g., 0.03 mole) dans une solution de 1.2 g. d'hydroxyde de soude dans 50 ml. d'eau distillée. On ajoute goutte à goutte

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de l'isocyanate de phényle (3.62 g., 0.03 mole) en maintenant la solution à la température de la chambre. La solution est agitée pendant environ 15 min. et ensuite acidifiée avec 15 ml. d'acide chlorhydrique concentré. On chauffe la solution sur un bain-marie bouillant pendant une heure, puis on l'évapore à sec sous pression réduite. Le résidu est recristallisé de l'alcool dilué. Rendement: 4 g., 61%. P. f. 97–98° C. Calculé pour $C_{12}H_{12}O_2N_2$: N, 12.9%. Trouvé: N, 12.8%.

3-Phényl-5-(2,3-dichloropropyl)hydantoïne

A la température de la chambre, on fait barbotter du chlore gazeux dans une solution de 3-phényl-5-allylhydantoïne (2 g., 0.0092 mole) dans 100 ml. de chloroforme. Lorsque la solution est complètement saturée de chlore, on l'évapore à sec sous pression réduite. On cristallise le résidu huileux de l'alcool dilué. Rendement: 1 g., 38%. P. f. 142° C. Calculé pour $C_{12}H_{12}O_2N_2Cl_2$: N, 9.78%; Cl, 24.5%. Trouvé: N, 9.28%; Cl, 20.3%.

3-Phényl-5-(2,3-dibromopropyl)hydantoïne

Dans un ballon à large col de 300 ml., on dissout de la 3-phényl-5-allylhydantoïne (2 g., 0.0092 mole) dans 100 ml. de chloroforme. A la température de la chambre, on ajoute goutte à goutte du brome (1.5 g., 0.0094 mole). L'addition terminée, on évapore la solution à sec sous pression réduite. On recristallise le résidu de l'alcool dilué. Rendement: 2.75 g., 79%. P. f. 130–135° C. Calculé pour $C_{12}H_{12}O_2N_2Br_2$: N, 7.45%; Br, 42.5%. Trouvé: N, 7.46%; Br, 42.0%.

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THE VOLATILIZATION OF PLUTONIUM FROM NEUTRON-IRRADIATED URANIUM[1]

By D. E. McKenzie

ABSTRACT

The volatilization of plutonium from neutron-irradiated uranium has been examined at 1540°, 1650°, and 1769°C. The observed rates of evaporation of plutonium have been compared with calculated rates based on the Langmuir equation and Raoult's law. Experimental and calculated results agree within the precision of the experimental measurements, indicating that the plutonium in neutron-irradiated uranium follows the ideal solution laws.

INTRODUCTION

In some types of nuclear reactors uranium metal is used as fuel. The processing of the resulting neutron-irradiated uranium and return of the separated plutonium and uranium to the reactor may become important if such reactors are to produce economic power. Current processing methods require dissolution of the neutron-irradiated uranium and solvent extraction or ion exchange techniques to achieve the separation (1, 4). The uranium metal for re-irradiation must be prepared from the resulting aqueous solution. Alternative separation methods, in which uranium is retained as metal throughout, may offer advantages.

One possible method is the volatilization of plutonium from the uranium. This technique is suggested by the fact that, at, for example, 1540°C., the vapor pressure of plutonium (5) is 300 times that of uranium (6). This paper describes an investigation of the rate of evaporation, in vacuum, of plutonium from neutron-irradiated uranium. The results are in qualitative agreement with those obtained at the North American Aviation Laboratories in Downey, California (3).

EXPERIMENTAL

Materials and Apparatus

Neutron-irradiated uranium was obtained from rods which had been irradiated for various periods in the NRX reactor. The beryllia crucibles which were of the vertical-wall type were obtained from the Atomic Energy Research Establishment at Harwell, England. The evaporating area of a melt was calculated from the average of a number of diameter measurements of each crucible.

The apparatus for the distillation is illustrated in Fig. 1. The uranium was heated by a tungsten resistance coil, surrounded by beryllia thermal shields and molybdenum radiation shields. The assembly was mounted in a glass bulb which was evacuated by diffusion and mechanical pumps through a trap cooled by liquid air. The pumping equipment gave pressures of less than

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5×10^{-5} mm. of Hg in the system when the charge was at temperature. The system was contained in a dry box in which the glass bulb was surrounded by lead.

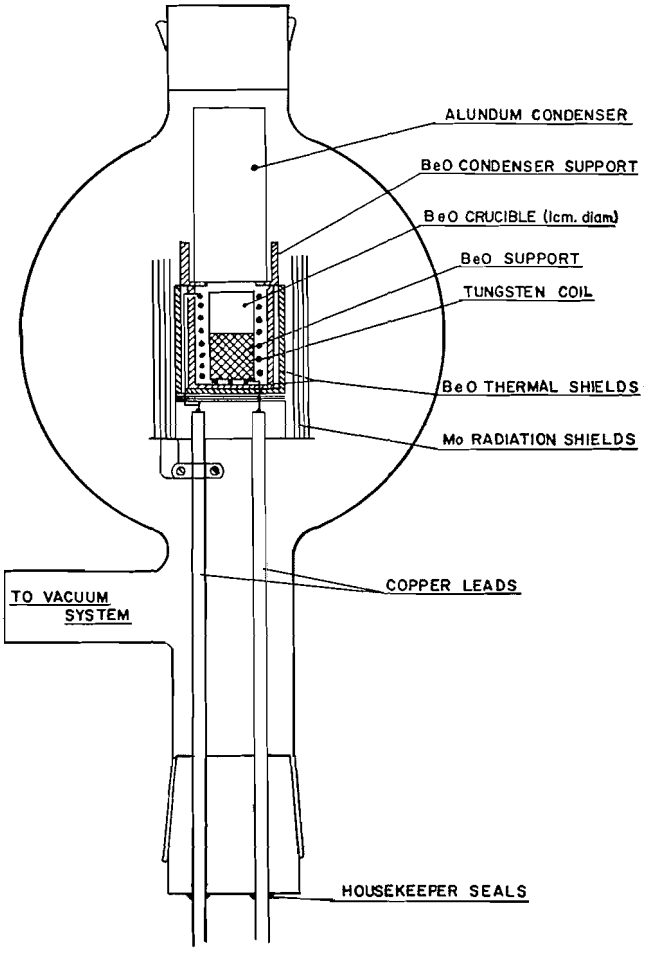

FIG. 1. Diagram of bulb and crucible assembly.

Distillations were carried out at 1540°, 1650°, and 1769°C. The temperatures 1540° and 1769°, the melting points of iron and platinum respectively, were reproduced by careful determinations of the power required to melt these metals in the crucible assembly. An interpolation of these values gave the power required for 1650°. The coils were always restandardized after two or three runs. A constant temperature during a run was maintained by observing the uranium charge with an optical pyrometer which was sighted through an optical window in the top ground-glass joint and a hole in the condenser. The maximum error in the temperature is ±15°C.

Procedure

The procedure for an experiment was as follows: A piece of neutron-irradiated uranium was etched in nitric acid to remove at least 25% of its

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weight for a reference solution. The remaining uranium was washed with water and with acetone before being placed in a beryllia crucible and put in the apparatus. The bulb was pumped down to a pressure of 10^{-6} mm. of Hg and power applied to the coil to degas the crucible and associated shields. The uranium was then heated to temperature to perform the distillation. The pressure in the system did not exceed 10^{-4} mm. of Hg during the degassing operation.

After distillation the charge was cooled to room temperature and the vacuum broken. The uranium residue was removed from the crucible and dissolved in nitric acid. Also the crucible was leached in nitric acid. These solutions and the reference solution were analyzed for plutonium by standard radiochemical procedures.

RESULTS

The data for the various runs are given in Table I. The total amount of plutonium distilled was determined from the plutonium content of the original uranium and the plutonium content of the uranium residue. Only that portion

TABLE I

DATA FOR PLUTONIUM DISTILLATIONS

Run No.	Wt. U (gm.)	Time (hr.)	Area (cm.²)	Pu distribution (% original)		
				Residue	Crucible	Condenser
Temperature = 1540°C.						
92	3.972	2.75	0.581	65.7	7.0	27.3
101	2.464	3.61	0.441	56.5	16.3	27.2
103	2.022	7.31	0.490	31.0	33.8	35.2
104	2.362	9.00	0.528	8.4	54.2	37.4
109	2.044	10.00	0.441	23.0	33.9	43.1
102	1.446	7.50	0.478	4.8	42.2	53.0
110	2.183	14.00	0.540	4.4	42.4	53.2
117	1.442	10.68	0.554	4.3	50.8	44.9
Temperature = 1650°C.						
81	3.460	0.82	0.581	67.1	7.7	25.2
85	4.229	2.00	0.528	38.0	25.2	36.8
82	4.017	1.75	0.581	32.6	33.6	33.8
83	4.307	3.67	0.515	25.8	35.8	38.4
84	4.027	4.27	0.586	13.4	37.4	49.2
107	1.841	3.58	0.430	3.9	40.0	56.1
106	3.393	10.37	0.407	4.3	34.7	61.0
108	3.157	7.62	0.515	1.9	40.2	57.9
116	5.487	13.58	0.502	2.0	25.5	72.5
Temperature = 1769°C.						
89	3.454	0.40	0.465	35.7	24.8	39.5
90	3.723	0.75	0.609	24.2	28.1	47.7
119	2.179	0.61	0.708	4.1	46.4	49.5
120	2.005	0.85	0.650	1.5	51.5	47.0
121	1.838	1.07	0.622	2.1	64.4	33.5

of the distilled plutonium that collected on the sides of the crucible was recovered for analysis. This plutonium fraction is due to distillation since in one run, the top of the crucible, which had been sawed directly above the uranium residue, contained essentially all the plutonium found in the crucible.

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Plutonium balances were made in two runs by crushing and leaching the alundum condenser. In run 116, 94% of the original plutonium was recovered and in run 117, 85% was recovered.

DISCUSSION

The results have been correlated with theory in the following manner. W, the theoretical rate of evaporation per unit area of a pure substance in vacuum, is given by the Langmuir equation (2)

[1] $$W = 0.0583\, p_0\sqrt{(M/T)}$$

where W has the units gm. cm.$^{-2}$ sec.$^{-1}$ for the constant 0.0583,

M = the molecular or atomic weight of the vaporizing species, and

p_0 = the vapor pressure of the pure substance in mm. of Hg at the temperature T°K.

In the derivation of this equation a clean evaporating surface and uniform temperature in the melt are assumed. Although these conditions, in particular the clean surface, are not strictly adhered to, the equation will be used for the present experiments.

To apply the Langmuir equation to the evaporation of a particular component from a solution it is necessary to replace the vapor pressure of the pure substance, p_0 in equation [1], by the partial pressure of that component above the solution. For dilute metallic solutions the solute (i.e. the less concentrated component) generally obeys Henry's law which defines this partial pressure as

[2] $$p = k\, n$$

where k is a constant and n is the mole fraction of the component in solution. If the component obeys Raoult's law then k is equal to p_0. For convenience in comparing the results with Henry's and with Raoult's laws we introduce a new constant k' such that $k = k'p_0$. Thus, assuming the component follows Henry's law, the Langmuir equation for the evaporation of that component from a solution becomes

[3] $$W = 0.0583\, k'\, p_0\, n\sqrt{(M/T)}.$$

Equation [3] has been integrated, for application to the distillation of plutonium from neutron-irradiated uranium, with the following result:

[4] $$\log Y/Y_0 = -\left(\frac{0.0583}{2.303}\, p_0\sqrt{(M/T)}\right) k'\, \frac{tA}{U_0}$$

where Y/Y_0 = the fraction of the original plutonium in the residue,

t = the time of distillation in seconds,

A = the evaporating area in cm.^{2}, and

U_0 = the initial weight of the uranium in grams.

It was assumed in the integration that k' and U_0 are constants, i.e. k' is independent of plutonium concentration in the range studied, and the amount of uranium distilled is a negligible fraction of the original charge. The mole fraction of plutonium was assumed to be weight of plutonium/weight of uranium. In addition, the assumptions in applying [4] are (1) neutron-

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irradiated uranium behaves as a binary solution of plutonium in uranium and (2) plutonium distills in monatomic form.

The experimental results have been correlated with equation [4] by (1) assuming Raoult's law, i.e. $k' = 1$, and calculating a theoretical value for the plutonium distilled and (2) assuming Henry's law and calculating a value for k'. The equation $\log p_{mm} = 7.895 - 17590/T$ has been used for the vapor pressure of pure plutonium (5). The correlations are summarized in Tables II, III, and IV (the units of time have been changed to hours). The experi-

TABLE II

COMPARISON OF EXPERIMENTAL AND CALCULATED DISTILLATIONS OF PLUTONIUM FOR 1540°C.
$\log Y/Y_0 = -0.516(tA/U_0)k'$

Run No.	Initial Pu conc. (wt.%)	Time × area / Wt. of U (hr. cm.^{2} gm.$^{-1}$)	Pu distilled (% original)		k'
			Calc. ($k' = 1$)	Exptl.	
92	0.047	0.403	38.0	34.3	0.9
101	0.014	0.646	53.6	43.5	0.7
103	0.0068	1.77	87.8	69.0	0.6
104	0.0055	2.01	90.9	91.6	1.0
109	0.034	2.16	92.3	77.0	0.6
102	0.024	2.48	94.7	95.2	1.0
110	0.054	3.46	98.4	95.6	0.8
117	0.11	4.11	99.2	95.7	0.6

TABLE III

COMPARISON OF EXPERIMENTAL AND CALCULATED DISTILLATIONS OF PLUTONIUM FOR 1650°C.
$\log Y/Y_0 = -1.797(tA/U_0)k'$

Run No.	Initial Pu conc. (wt.%)	Time × area / Wt. of U (hr. cm.^{2} gm.$^{-1}$)	Pu distilled (% original)		k'
			Calc. ($k' = 1$)	Exptl.	
81	0.031	0.138	43.5	32.9	0.7
85	0.086	0.250	64.4	62.0	0.9
82	0.082	0.253	64.9	67.4	1.1
83	0.052	0.439	83.7	74.2	0.7
84	0.066	0.622	92.4	86.6	0.8
107	0.054	0.836	96.8	96.1	1.0
106	0.0038	1.24	99.4	95.7	0.6
108	0.024	1.24	99.4	98.1	0.8
116	0.020	1.24	99.4	98.0	0.8

TABLE IV

COMPARISON OF EXPERIMENTAL AND CALCULATED DISTILLATIONS OF PLUTONIUM FOR 1769°C.
$\log Y/Y_0 = -5.950(tA/U_0)k'$

Run No.	Initial Pu conc. (wt.%)	Time × area / Wt. of U (hr. cm.^{2} gm.$^{-1}$)	Pu distilled (% original)		k'
			Calc. ($k' = 1$)	Exptl.	
89	0.067	0.054	52.8	64.3	1.4
90	0.085	0.123	81.4	75.8	0.8
119	0.24	0.198	93.4	95.9	1.2
120	0.13	0.275	97.7	98.5	1.1
121	0.011	0.361	99.3	97.9	0.8

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mental results are compared with calculations based on Raoult's law in Figs. 2, 3, and 4 where log Y/Y_0 is plotted against tA/U_0. The effect of an uncertainty in temperature of ± 15°C. is shown in these figures.

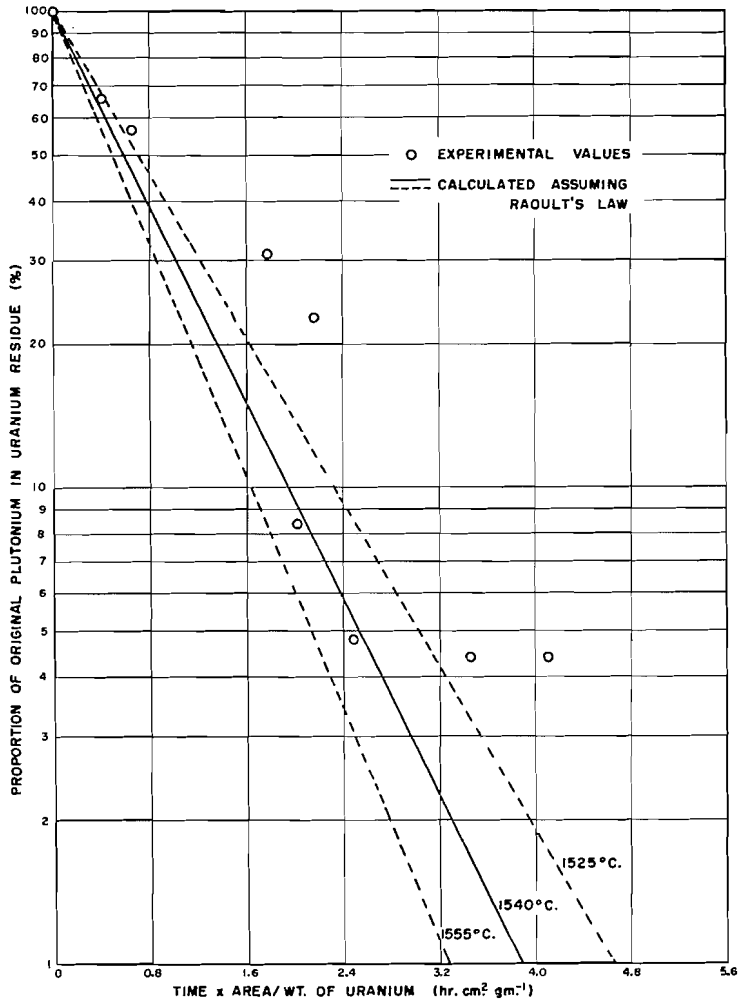

FIG. 2. Comparison of calculated and experimental results for runs at 1540°C. The dotted lines indicate the effect, on the calculations, of an error of ± 15°C. in temperature.

The quantity k' is the activity coefficient of plutonium in neutron-irradiated uranium. Its variation with temperature can be related to the heat of solution of plutonium in this material. However, the estimated error in the values of k' obtained by the present procedures is about $\pm 25\%$ (the uncertainty in temperature alone results in an error of $\pm 17\%$). The average value of k' for each temperature deviates from unity by less than this experimental error.

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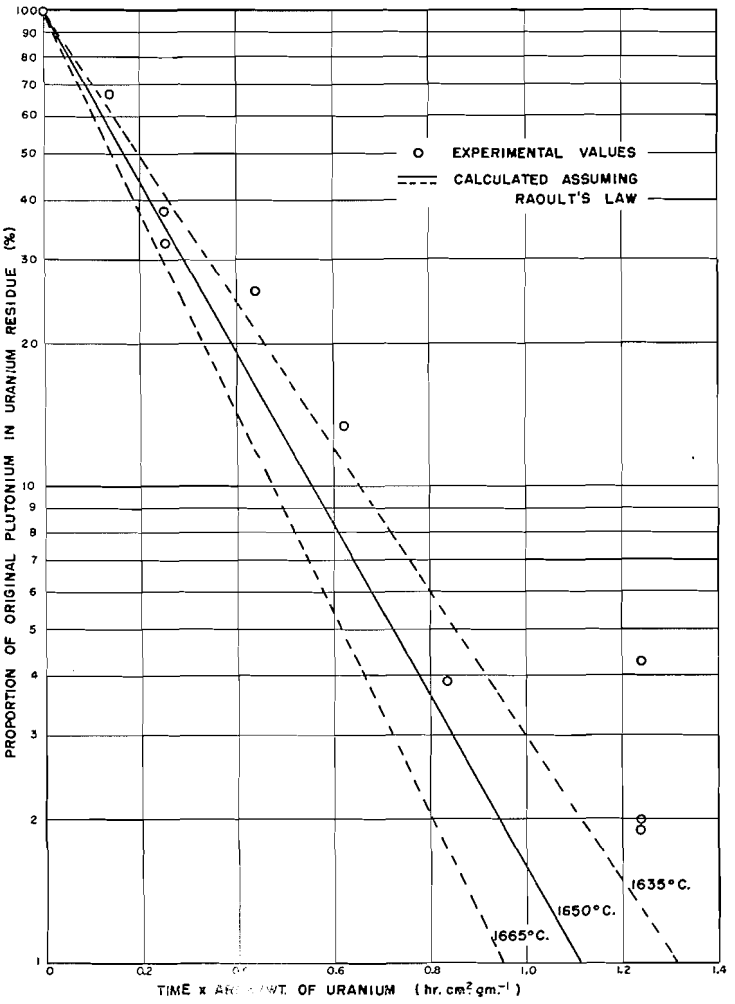

FIG. 3. Comparison of calculated and experimental results for runs at 1650°C.

In addition, no effect due to varying plutonium concentrations is observed. Thus, for these temperatures and concentrations, it is concluded that plutonium in neutron-irradiated uranium forms essentially an ideal solution.

This conclusion might have been predicted from the proximity of plutonium to uranium in the actinide series. Deviations of k' from unity, if real, are probably associated with assumptions made in the treatment of the data. Uranium, since it is an excellent "getter" for oxygen, would not be expected to have a clean evaporating surface. Also plutonium may form high melting point compounds with one or more of the fission products. Both of these effects would lower the evaporation rate from that predicted from the Langmuir equation and Raoult's law.

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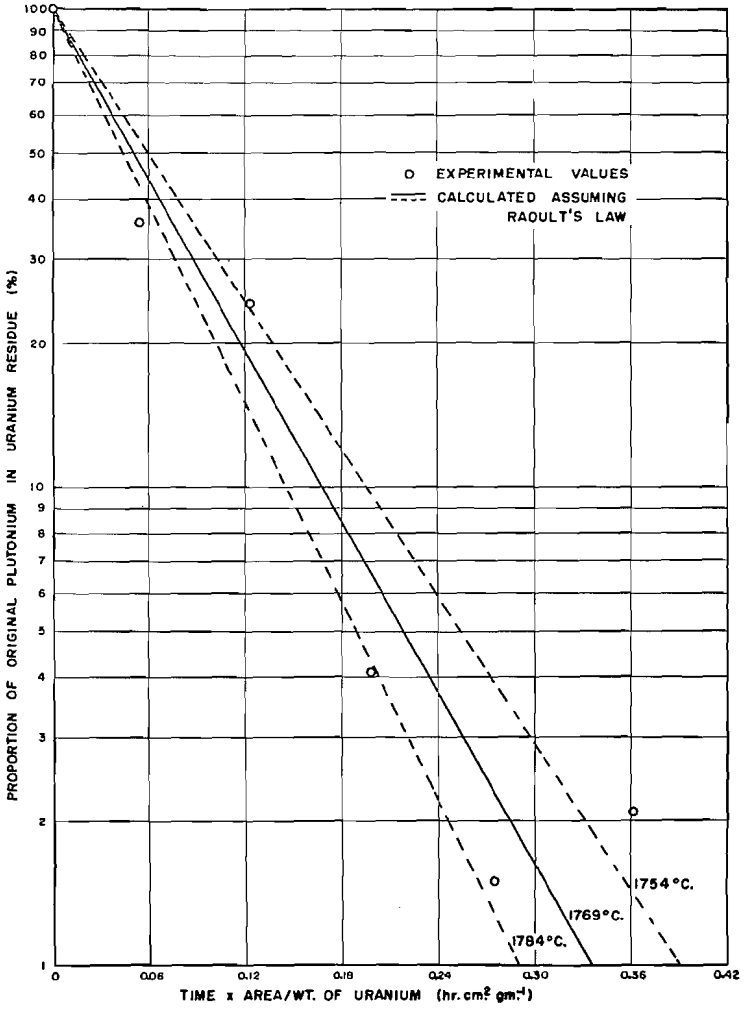

FIG. 4. Comparison of calculated and experimental results for runs at 1769°C.

ACKNOWLEDGMENT

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THE ELUCIDATION OF THE STRUCTURE OF HYOCHOLIC ACID[1]

By P. Ziegler

ABSTRACT

Hyocholic acid, a new bile acid isolated from hog bile, was identified as 3(α), 6(α),7(α)-trihydroxycholanic acid.

The bile acids are the main constituents of animal bile where they are usually found in conjugation with amino acids. In the past it has been the practice to saponify bile under rigorous alkaline conditions prior to isolation of the constituent bile acids and, in this manner, the compositions of the bile acid mixtures from a large number of animals were determined. Hog bile proved to be an exception despite a considerable amount of effort, and the greater portion of the saponified hog bile solids could never be accounted for in the form of identifiable bile acids or their derivatives (7, 8). This has prompted a careful investigation of hog bile in these laboratories resulting in the isolation of a hitherto unknown acid which, according to established terminology, will be named hyocholic acid.

By the procedure of isolation (to be reported in more detail at a later date) hyocholic acid was obtained as the methylated and acetylated derivative which gave satisfactory analyses for I and also was found, by acetate determination, to contain three moles of acetate per mole of steroid. This compound was transparent to ultraviolet from 220 to 400 mμ, failed to react with tetranitromethane or ketone reagents, and, on infrared examination, exhibited the characteristic bands of the carbomethoxy and acetate groups. Saponification of I afforded hyocholic acid (II) which analyzed correctly for a trihydroxycholanic acid; it was not identical with the widely distributed cholic acid and a literature survey failed to reveal any bile acid with properties similar to II. It was later found that the methyl ester of hyocholic acid gave a positive Malaprade test, indicating that at least two of the three hydroxyl groups were adjacent to each other, an arrangement unknown in the natural bile acids.

Hyocholic acid (II) was then oxidized with chromic acid to give, after methylation, 3-ketothilobilianic acid trimethyl ester (III), not previously described. This compound gave a positive Zimmermann reaction and analyzed correctly for three methoxyl groups. Obviously the carbon–carbon bond of the vicinal glycol was ruptured giving rise to two new carboxyl groups, while the third hydroxyl function was oxidized to a ketone. This proved that all three hydroxyl groups were secondary alcohols and that one of these was isolated from the glycol structure and not adjacent to it. The positive Zimmermann reaction showed that the ketone was not located at positions 6, 7, or 12 of the nucleus. It now remained to determine which of the rings had broken during the oxidation; this would locate at once the positions of the two vicinal

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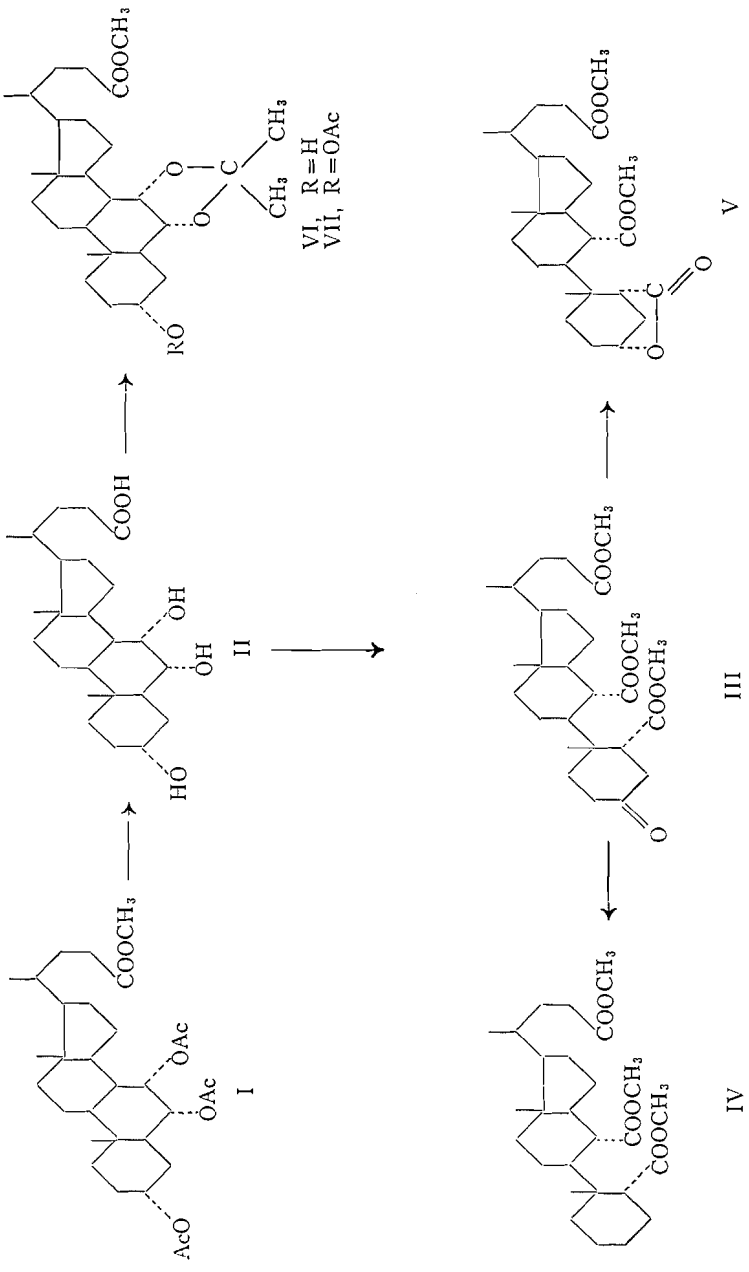
Contribution from the Research and Development Laboratories of Canada Packers Ltd., Toronto, Ont.

hydroxyl groups. It was then assumed that the isolated hydroxyl group in hyocholic acid (II) was present at C-3, because all naturally occurring bile acids have this characteristic grouping and because the positive Zimmermann test exhibited by III lent further evidence for that, although this did not



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constitute a rigid proof. That assumption at once eliminated ring A as the site of the glycol which previously was shown to be removed by at least two carbon atoms from the third hydroxyl group. Ring C also could be excluded because all possible isomers of 3(α),11,12-trihydroxycholanic acid are synthetic products described in the literature (2, 11) and none of these compounds had the physical properties of hyocholic acid. That left rings B and D as the only possible locations for the vicinal hydroxy groups. Ring D seemed an unlikely prospect since hydroxylation in that ring is not known to occur in bile acids. Clearly then ring B was suspected and circumstantial evidence could be derived from the fact that hog bile contains 20% of 3(α),6(α)-dihydroxycholanic acid and an appreciable quantity of 3(α),7(α)-dihydroxycholanic acid. These acids (hyo- and cheno-desoxycholic acid respectively) are produced in the liver from cholesterol and it seemed reasonable to think that the enzymes responsible for hydroxylation at C-6 and C-7 could also produce compounds that are doubly hydroxylated, giving rise to the 6,7-vicinal glycol.

Definite proof for this was then obtained from two products derived from 3-ketothilobilianic acid trimethyl ester (III). This compound was reduced by Huang-Minlon's modification of the Wolff–Kishner reduction (4) to give, after methylation, IV which was found to be identical with the thilobilianic acid trimethyl ester prepared by Wieland (10). Sodium borohydride reduction of III and subsequent esterification gave V which was found to contain only two methoxyl groups. Infrared examinations showed conclusively the presence of a five-membered lactone ring by the very characteristic absorption bands at 940 and 1775 cm.$^{-1}$ (3, 5). This lactone (V) has also been prepared by Japanese workers (13) by nitric acid oxidation of 3(α)-acetoxy-6(or 7)-ketocholanic acid.

The above experiments furnished proof for the location of the hydroxyl groups at positions 3, 6, and 7. It now remained to determine the stereochemical configuration of these groups. It was found that hyocholic acid did not give an insoluble digitonide, which indicated that the hydroxyl group at C-3 was in the α-position. Conclusive evidence for this was also obtained from V which was identical with the lactone obtained by the Japanese investigators (13) whose starting material contained the 3(α)-hydroxy group; during their sequence of reactions no change took place involving in any way the stereochemistry of the alcohol group. In our hands, V was obtained by sodium borohydride reduction of the ketone III and it is well known (6) that such reductions yield predominantly 3(α)-hydroxy compounds in the A/B *cis* series and 3(β)-hydroxy analogues in the A/B *trans* series. Furthermore, the presence of the lactone in V is also excellent proof not only for the α-configuration of the 3-hydroxy group but also for the A/B *cis* junction. Five-membered lactones are planar and as such require that their two bonds, which are the links to ring A, be in the same plane, either both α or both β. There is however a difference between the two as regards ease of formation. Lactones of the α-type such as V form spontaneously from the corresponding hydroxy acids which cannot be isolated (3, 13); on the other hand, 3(β)-hydroxy-5(β)-carbohydroxy steroids exist as such and lactonize only after

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treatment with hot acetic anhydride or under similar conditions (12). In our work the hydroxy compound was not isolated but only the lactone which must have formed during acidification in the cold of the alkaline sodium borohydride reaction mixture. Clearly this represents ample support for the α-configuration of the lactone in V.

The hydroxyl groups at C-6 and C-7 can exist in four different stereochemical positions in two of which they are in the same plane ($6\alpha,7\alpha$ or $6\beta,7\beta$). It is known that only those vicinal glycols in which the alcoholic functions are in the same plane form acetonides (9). The methyl ester of hyocholic acid (II) was therefore treated with acetone and *p*-toluenesulphonic acid, but no crystalline substance could be obtained. The residue was then acetylated and the products chromatographed on alumina. Nearly all the material was eluted with benzene but again no crystals could be isolated. The benzene fraction was found to contain only one acetate group per mole of steroid. Another portion of the benzene eluate was then examined in the infrared and no trace of a free hydroxyl group could be detected. Therefore the acetonides VI and VII must have been formed and the hydroxyl groups in II are in the same plane. Additional support for acetonide formation was also obtained by refluxing VII with acetic acid which decomposed the acetonide to give acetone. After dilution with water, the mixture was distilled and the distillate gave a positive iodoform test.

The above experiments then left only two possibilities for the structure of hyocholic acid, the one having the glycol at $6(\alpha),7(\alpha)$, the other at $6(\beta),7(\beta)$. A differentiation between these two can be made on the basis of molecular rotation data which have recently been very useful in structure elucidation of steroids. The fundamental concept consists of the usually valid claim that a given functional group at a given location and configuration will always contribute the same amount to the molecular rotation of the whole molecule; or, in other words, the molecular rotation of a compound is the algebraic sum of the rotatory contributions of the constituent parts of the molecule. This holds true only if there are no "vicinal effects" which result from the interaction of functional groups which are situated close to each other in space.

From the data of Barton and Klyne (1) and from our own work, we have determined the individual rotatory contributions (all values in alcohol) of hydroxyl groups in ring B of the normal bile acid series. Lithocholic acid was found to have $[M]_D$ +121 and from these values the approximate molecular rotations of the two alternative structures for hyocholic acid should be as given below:

$[M]_D$ of $3(\alpha),6(\alpha),7(\alpha)$-trihydroxycholanic acid $= +121-62-72 = -13$,

$[M]_D$ of $3(\alpha),6(\beta),7(\beta)$-trihydroxycholanic acid $= +121+24+103 = +248$.

Hyocholic acid was found to have $[M]_D$ +19, which agrees more closely with the $6(\alpha),7(\alpha)$-structure, though the approximation is not nearly as satisfactory as would be expected if there were no "vicinal effects". But it must be realized immediately that such "vicinal effects" are operative in hyocholic acid because of the interaction within the glycol grouping. An examination of the above data reveals that both the $6(\alpha)$- and the $7(\alpha)$-hydroxy contributions are

negative, while the opposite configurations give positive increments. It is reasonable to predict that, where "vicinal effects" exist, the numerical value of a rotatory contribution will be smaller than the calculated "non-vicinal" value, provided the latter has a numerical value which is not close to zero. If this is applied to the 6(α),7(α)-structure, the $[M]_D$ value would come close to +19 which was determined experimentally for hyocholic acid. At the same time the vicinal contributions of the two hydroxyl groups, though numerically reduced, would not change in sign (negative). On the other hand, in the 6(β), 7(β)-structure, the combined "non-vicinal" contributions are +127 which would have to change to −102 to accommodate the experimentally determined value of $[M]_D$ +19. This is extremely unlikely.

Besides the above evidence obtained from rotation data, there is also available some biogenetic indication for the α-configuration of the hydroxyl groups in ring B. An examination of the known constituents of hog bile shows that some compounds have hydroxyl groups at 6(α) or 7(α), but not a single hog bile acid has a hydroxyl group in the β-configuration in ring B.

From the data presented it was concluded that hyocholic acid is 3(α),6(α), 7(α)-trihydroxycholanic acid.

EXPERIMENTAL[2,3,4]

The Isolation of Methyl Hyocholate Triacetate (I)

Hog bile (1 liter) was refluxed with sodium hydroxide (100 gm.) for 60 hr. The solution was then acidified, extracted with ethyl acetate, and the solvent extract evaporated to a small volume. After cooling, the resulting precipitate was filtered off to yield 55 gm. of material, m.p. 150–160°C. This was treated with ethereal diazomethane and the crude methyl esters were crystallized from benzene to provide methyl hyodesoxycholate – benzene complex (23 gm.). The filtrate was evaporated *in vacuo* and the dry residue was then refluxed with pyridine (50 ml.) and acetic anhydride (250 ml.) for four hours. Evaporation of the solvents, extraction with ether, washing, and crystallization from hexane or iso-octane afforded crude I (15 gm.), m.p. 173–176°C. This was recrystallized several times from ether–hexane to give transparent, irregular plates, m.p. 188–190°C. and $[\alpha]_D^{20}$ +20.95° (*c*, 1.22, dioxane). Infrared absorption bands at 1040, 1165, 1225–1250, 1362, 1735–1740, and 2950 $cm.^{-1}$. This compound was found to contain 33.1% of acetate (calculated value = 32.27%). Analysis: Calcd. for $C_{31}H_{48}O_8$: C, 67.85; H, 8.82; O, 23.33. Found: C, 67.85, 67.81; H, 8.90, 8.88; O, 23.24, 23.34.

Hyocholic Acid (II)

Refluxing I with 4% methanolic potassium hydroxide for two hours provided, after several recrystallizations from ethyl acetate, prismatic needles of II, m.p. 183–185°C. and $[\alpha]_D^{24}$ +4.59° (*c*, 1.18, dioxane) and $[\alpha]_D^{25}$ +4.59° (*c*, 1.10, ethanol). Analysis: Calcd. for $C_{24}H_{40}O_5$: C, 70.55; H, 9.87; O, 19.58. Found: C, 70.78, 70.79; H, 9.75, 9.84; O, 19.64, 19.48.

[2]*The microanalyses were kindly performed by Mr. E. Thommen, Basel, Switzerland; the acetate determinations by Mr. C. K. Cross in our laboratories.*

[3]*The infrared examinations were made through the courtesy of Dr. G. D. Laubach of Ch. Pfizer & Co., Brooklyn, N.Y., and Miss Kirby of the Ontario Research Foundation, Toronto.*

[4]*The procedure for the isolation of I was developed in collaboration with Mrs. G. C. Buckley and Mr. A. A. Amos.*

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3-Ketothilobilianic Acid Trimethyl Ester (III) from II

Compound II (2 gm.) was dissolved in acetic acid (25 ml.) and there was then added over a period of one hour a solution of chromic acid (1.8 gm.) in water (1 ml.) and acetic acid (25 ml.). The temperature was kept at 15–20°C. during the addition and for 14 hr. thereafter. The excess oxidizing agent was destroyed by sodium bisulphite and the solvents were then removed *in vacuo* at 30°C. The residue was taken up in dilute sulphuric acid and ether, the aqueous phase was extracted two more times with ether, the combined ether extracts were washed with dilute acid, then with water, and finally dried and evaporated to dryness. After methylation with ethereal diazomethane, the residue was crystallized from ether–hexane to afford 854 mgm. of material, m.p. 130–137°C. Several recrystallizations from ether–hexane yielded prismatic needles, m.p. 140–142°C. and $[\alpha]_D^{25}$ −5.05° (*c*, 0.29, dioxane). This compound (III) gave a positive Zimmermann reaction, failed to give a coloration with alcoholic ferric chloride, tetranitromethane, or triphenyltetrazolium, and did not absorb in the ultraviolet region. Infrared examination revealed strong bands at 1165, 1220, 1445, 1730, and 2930 $cm.^{-1}$ and several weaker bands in the region of 1100 to 1400 $cm.^{-1}$. Analysis: Calcd. for $C_{27}H_{42}O_7$: C, 67.75; H, 8.85; OCH_3, 19.45. Found: C, 67.81, 67.93; H, 8.82, 8.93; OCH_3, 19.33, 19.35.

Thilobilianic Acid Trimethyl Ester (IV) from III

Compound III (250 mgm.) was dissolved in diethylene glycol (8 ml.), then a hot solution of potassium hydroxide (2 gm.) in the same solvent (12 ml.) was added. After addition of 85% hydrazine hydrate (3 ml.), the solution was refluxed for one hour, the condenser was then set downwards, and the solution distilled until the internal temperature had reached 200°C. The solution was then refluxed for two hours, cooled, diluted with water, acidified with hydrochloric acid, and extracted three times with ether. The solvent extracts were washed first with dilute acid, then with water, and subsequently dried over sodium sulphate and evaporated to dryness to yield an amorphous residue (162 mgm.). This was methylated with diazomethane, then crystallized from aqueous methanol to give 82 mgm. of impure IV, m.p. 95–100°C. Two recrystallizations from iso-octane furnished IV, m.p. 108–109°C. and $[\alpha]_D^{24}$ −13.6° (*c*, 0.695, dioxane). Wieland (10) cites m.p. 109°C. Analysis: Calcd. for $C_{27}H_{44}O_6$: C, 69.79; H, 9.55; O, 20.66; OCH_3, 20.03. Found: C, 69.92; H, 9.36; O, 21.39; OCH_3, 19.84.

3(α)-Hydroxythilobilianic Acid – 3,5-Lactone Dimethyl Ester (V) from III

Compound III (100 mgm.) was dissolved in methanol (15 ml.) and the solution was cooled to 5°C. There was then added, in five portions, sodium borohydride (60 mgm.). The solution was kept at 20°C. overnight; it was then diluted and acidified and the products extracted with ether several times. Working up in the usual way, methylating, and crystallizing from ether–hexane afforded 47 mgm. of substance, m.p. 152–153°C. This was dissolved in ether–hexane, the solution heated to remove the ether and cooled; in this manner, irregular, transparent plates, m.p. 157–159°C. and $[\alpha]_D^{24}$ −18.9° (*c*, 0.61, dioxane), were obtained. Infrared examination showed the typical

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five-membered lactone absorption at 940 and 1775 cm.$^{-1}$ as well as bands at 1725 and 1750 cm.$^{-1}$. This compound did not give a color reaction in the Zimmermann test. Analysis: Calcd. for $C_{26}H_{40}O_6$: C, 69.61; H, 8.99; O, 21.40; OCH_3, 13.84. Found: C, 69.82; H, 9.08; O, 21.57; OCH_3, 13.52.

Acetonide Formation (VI and VII)

Hyocholic acid (250 mgm.) was methylated with diazomethane and the excess reagent was removed *in vacuo*. After thorough drying, the residue was dissolved in dry acetone (20 ml.), *p*-toluenesulphonic acid (50 mgm.) was added, and the stoppered flask kept at 20–25°C. for 20 hr. The solution was neutralized with sodium bicarbonate, diluted with water, and exhaustively extracted with ether. The solvent extracts were washed, dried, and evaporated to dryness to give a residue (284 mgm.) which could not be induced to crystallize, despite chromatography on alumina.

This residue (VI) was then acetylated at 20°C. with pyridine (3 ml.) and acetic anhydride (5 ml.) for 17 hr. The solvents were removed *in vacuo* at 30°C. and again the residue did not crystallize. It was dissolved in benzene (25 ml.), poured over a column of alumina (10 gm.) and the adsorbent washed with benzene (100 ml.). The combined benzene eluates were evaporated to dryness to give the residue (223 mgm.) which was used for the subsequent tests.

(*a*) Infrared analysis showed that the material did not contain any free hydroxyl groups. The main bands were at 880, 1040, 1050, 1260, 1370, 1385, 1465, 1740, and 2875 cm.$^{-1}$.

(*b*) 45.8 mgm. of the residue required 4.03 ml. of 0.02438 *N* sodium hydroxide in the acetate determination; this indicates the presence of 12.7% acetate in VII. The calculated value (for one mole of acetate) is 11.7%.

(*c*) *Iodoform test.*—Approximately 100 mgm. of amorphous VII was dissolved in acetic acid (10 ml.) and the solution refluxed for one-half hour. The solution was diluted with water (40 ml.) and the resulting mixture distilled until 10 ml. of distillate was collected. The distillate was made strongly alkaline by addition of 10% sodium hydroxide and then the potassium iodide – iodine reagent was added. An immediate precipitation of yellow iodoform resulted. A blank did not produce any precipitate.

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SYNTHESES AND ABSORPTION SPECTRA OF 1-CHLOROPHENYL-3-PHENYL-4-ALKYL-5-PYRAZOLONES AND PYRAZOLONES-4-C^{14} [1]

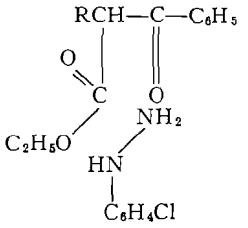
By Paul E. Gagnon, Jean L. Boivin,[2] and Yvon Laflamme[3]

ABSTRACT

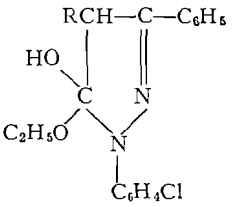
Monosubstituted benzoylacetic esters $C_6H_5COCH(R)CO_2C_2H_5$ (R = H, C_nH_{2n+1} (n = 1 to 9), and $C_6H_5CH_2$) obtained by the condensation of n-alkyl halides with ethyl benzoylacetate were reacted with o-, m-, and p-chlorophenylhydrazines to give 1-chlorophenyl-3-phenyl-4-alkyl-5-pyrazolones. Pyrazolones-4-C^{14} were prepared by the action of the same hydrazines on ethyl benzoylacetate-α-C^{14} obtained from benzoyl chloride and ethyl malonate-2-C^{14}. Their activities were 801, 894, and 847 c./min. respectively. The ultraviolet and infrared absorption spectra of all the pyrazolones were determined and the most probable structures ascribed to the compounds.

INTRODUCTION

The condensation of hydrazine and its monosubstituted derivatives with β-keto esters (I) gives by elimination of water a hydrazone (II) which, by elimination of another molecule of water, produces an alkoxypyrazole (III) or a pyrazolone (IV) by elimination of alcohol.



I



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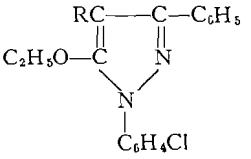
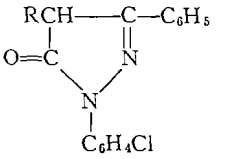


III



IV

The main product is an ethoxypyrazole when the reagents are heated in acid media and a pyrazolone when they are heated alone.

[1]*Manuscript received December 23, 1955.*

Contribution from the Department of Chemistry, Laval University, Quebec, Que. This paper constitutes part of a thesis submitted to the Graduate School, Laval University, in partial fulfillment of the requirements for the degree of Doctor of Science.

[2]*Defence Research Board, C.A.R.D.E., Valcartier, Que.*

[3]*Graduate Student, holder of a Canadian Industries Limited Research Scholarship in 1953–1954, and of a National Research Council of Canada Studentship in 1954–1955.*

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TABLE I

1-*o*-CHLOROPHENYL-3-PHENYL-4-MONOALKYL-5-PYRAZOLONES $RC_{15}H_{10}ON_2Cl$

R	M.p.,°C.	Yield, %	Formula	Analysis						Ultraviolet absorption maxima	
				Calculated, %			Found, %				
				C	H	N	C	H	N	Å	log E_m
H	170–171	86	$C_{15}H_{11}ON_2Cl$	66.54	4.09	10.34	66.35	4.18	10.47	3200 2540	3.798 4.292
CH_3	171–172	70	$C_{16}H_{13}ON_2Cl$	67.48	4.60	9.83	67.33	4.52	9.76	3050 2620	3.896 4.341
C_2H_5	121–122	67	$C_{17}H_{15}ON_2Cl$	68.33	5.06	9.37	68.27	5.07	9.36	3100 2580	3.633 4.376
C_3H_7	137–138	53	$C_{18}H_{17}ON_2Cl$	69.26	5.47	8.95	69.13	5.45	9.16	3100 2600	3.473 4.343
C_4H_9	130–131	74	$C_{19}H_{19}ON_2Cl$	69.82	5.85	8.57	69.80	5.90	8.81	3100 2600	3.718 4.349
C_5H_{11}	120–121	55	$C_{20}H_{21}ON_2Cl$	70.47	6.21	8.21	70.65	6.07	8.17	3100 2480	3.729 4.208
C_6H_{13}	122–123	51	$C_{21}H_{23}ON_2Cl$	71.07	6.53	7.89	70.94	6.47	8.07	3000 2600	3.873 4.172
C_7H_{15}	109–110	45	$C_{22}H_{25}ON_2Cl$	71.62	6.80	7.59	71.88	6.72	7.80	3050 2560	3.808 4.232
C_8H_{17}	103–104	56	$C_{23}H_{27}ON_2Cl$	72.13	7.10	7.31	72.18	7.04	7.60	2980 2600	3.751 4.246
C_9H_{19}	103–104	45	$C_{24}H_{29}ON_2Cl$	72.21	7.36	7.05	72.38	7.29	7.19	3100 2560	3.760 4.168
$C_6H_5CH_2$	157–158	78	$C_{22}H_{17}ON_2Cl$	73.22	4.75	7.76	73.17	4.71	7.64	3000 2620	3.398 4.283

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TABLE II

1-*m*-CHLOROPHENYL-3-PHENYL-4-MONOALKYL-5-PYRAZOLONES $RC_{15}H_{10}ON_2Cl$

R	M.p.,°C.	Yield, %	Formula	Analysis						Ultraviolet absorption maxima	
				Calculated, %			Found, %				
				C	H	N	C	H	N	Å	log E_m
H	108–109	81	$C_{15}H_{11}ON_2Cl$	66.54	4.09	10.34	66.56	4.13	10.32	3000 2600	3.970 4.394
CH_3	160–161	57	$C_{16}H_{13}ON_2Cl$	67.48	4.60	9.83	67.51	4.49	9.85	3050 2560	3.867 4.017
C_2H_5	105–106	64	$C_{17}H_{15}ON_2Cl$	68.33	5.06	9.37	68.17	5.06	9.39	3100 2520	3.438 4.394
C_3H_7	109–110	57	$C_{18}H_{17}ON_2Cl$	69.26	5.47	8.95	69.37	5.54	9.17	3000 2540	3.862 4.268
C_4H_9	119–120	69	$C_{19}H_{19}ON_2Cl$	69.82	5.85	8.57	69.97	6.05	8.61	2980 2540	3.403 4.119
C_5H_{11}	120–121	57	$C_{20}H_{21}ON_2Cl$	70.47	6.21	8.21	70.40	6.14	8.33	2980 2480	3.804 4.222
C_6H_{13}	140–141	49	$C_{21}H_{23}ON_2Cl$	71.07	6.53	7.89	71.05	6.57	8.10	3150 2500	3.559 4.366
C_7H_{15}	102–103	46	$C_{22}H_{25}ON_2Cl$	71.62	6.80	7.59	71.73	6.87	7.68	3100 2520	3.585 4.328
C_8H_{17}	111–112	52	$C_{23}H_{27}ON_2Cl$	72.13	7.10	7.31	71.85	7.03	7.45	2980 2480	3.457 4.322
C_9H_{19}	118–119	49	$C_{24}H_{29}ON_2Cl$	72.61	7.36	7.05	72.65	7.54	7.15	3100 2600	3.326 4.134
$C_6H_5CH_2$	161–162	62	$C_{22}H_{17}ON_2Cl$	73.22	4.75	7.76	73.31	4.71	7.81	2980 2520	3.642 4.108

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TABLE III

1-*p*-CHLOROPHENYL-3-PHENYL-4-MONOALKYL-5-PYRAZOLONES $RC_{15}H_{10}ON_2Cl$

R	M.p.,°C.	Yield, %	Formula	Analysis						Ultraviolet absorption maxima	
				Calculated, %			Found, %				
				C	H	N	C	H	N	Å	log E_m
H	161–162	64	$C_{15}H_{11}ON_2Cl$	66.54	4.09	10.34	66.56	4.23	10.56	3050 2520	3.723 4.197
CH_3	160–161	70	$C_{16}H_{13}ON_2Cl$	67.48	4.60	9.83	67.20	4.64	9.93	3150 2540	3.854 4.280
C_2H_5	117–118	67	$C_{17}H_{15}ON_2Cl$	68.33	5.06	9.37	68.15	5.18	9.50	3000 2480	3.842 4.131
C_3H_7	182–183	65	$C_{18}H_{17}ON_2Cl$	69.26	5.47	8.95	69.04	5.34	9.03	3000 2500	3.395 4.177
C_4H_9	125–126	49	$C_{19}H_{19}ON_2Cl$	69.82	5.85	8.57	69.70	5.74	8.77	3050 2560	3.778 4.220
C_5H_{11}	167–168	56	$C_{20}H_{21}ON_2Cl$	70.47	6.21	8.21	70.48	5.93	8.45	3150 2600	3.738 4.257
C_6H_{13}	152–153	45	$C_{21}H_{23}ON_2Cl$	71.07	6.53	7.89	71.32	6.44	8.12	3100 2520	3.740 4.249
C_7H_{15}	112–113	42	$C_{22}H_{25}ON_2Cl$	71.62	6.80	7.59	71.65	6.84	7.62	3150 2500	3.760 4.312
C_8H_{17}	117–118	49	$C_{23}H_{27}ON_2Cl$	72.13	7.10	7.31	72.11	7.15	7.34	3050 2580	3.454 4.297
C_9H_{19}	113–114	39	$C_{24}H_{29}ON_2Cl$	72.61	7.36	7.05	72.48	7.19	7.28	2960 2520	3.686 4.237
$C_6H_5CH_2$	165–166	50	$C_{22}H_{17}ON_2Cl$	73.22	4.75	7.76	73.25	4.88	7.89	2980 2480	3.469 4.332

One of the objects of the present investigation was to synthesize and to determine the structure of 1-chlorophenyl-3-phenyl-4-alkyl-5-pyrazolones. Another object was to prepare pyrazolones-4-C^{14}.

The starting esters used in the present work, the ethyl-α-monosubstituted-α-benzoylacetates, were prepared (9) by alkylation of ethyl benzoylacetate. The *o*-, *m*-, and *p*-chlorophenylhydrazines were prepared by diazotation of their respective anilines followed by reduction with sodium sulphite. The ethyl benzoylacetate-α-C^{14} was obtained by the condensation of benzoyl chloride with ethyl malonate-2-C^{14} and decarboxylation (1, 8).

The individual properties and analyses of all pyrazolones prepared are listed in Tables I, II, and III.

Ultraviolet Absorption Spectra

The ultraviolet absorption spectra of all pyrazolones were determined in alcohol solution. The results obtained are given in Tables I, II, and III and shown graphically in Figs. 1, 2, and 3.

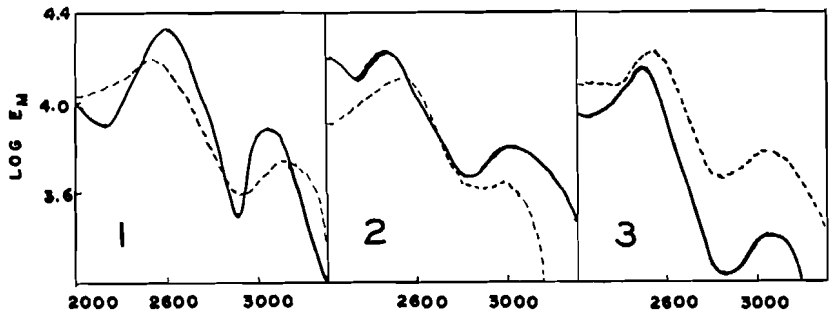
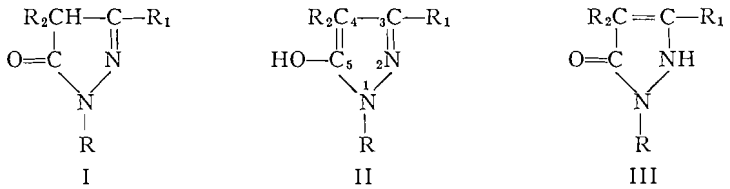


FIG. 1. Ultraviolet absorption spectra of 1-*o*-chlorophenyl-3-phenyl-4-alkyl-5-pyrazolones; ——— 4-methyl, --- 4-amyl.
FIG. 2. Ultraviolet absorption spectra of 1-*m*-chlorophenyl-3-phenyl-4-alkyl-5-pyrazolones; ——— 4-amyl, ---- 4-benzyl.
FIG. 3. Ultraviolet absorption spectra of 1-*p*-chlorophenyl-3-phenyl-4-alkyl-5-pyrazolones; ——— 4-propyl, ---- 4-butyl.

The pyrazolones have a tendency towards tautomerism and three structures may be postulated for the pyrazolones prepared.



The 4,4-dialkyl-pyrazolones as well as the pyrazolone dyes are derived from formula I. Formula II is invoked to explain the formation of alkoxypyrazoles and the formation of sodium salt. Formula III explains the easy methylation of the nitrogen atom 2.

The spectra exhibited by many pyrazolones have been studied intensively by many workers (2, 3, 4, 5, 6). These authors related the wavelength of the

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absorption band and its intensity to the position of the double bond in the ring. It was found that a high intensity maximum at short wavelength was indicative of a double bond between two carbon atoms while a low intensity maximum at longer wavelength corresponded to a double bond between the nitrogen atom 2 and the carbon atom 3. The presence of two maxima for the same compound was attributed to the presence of two tautomeric forms (7).

The spectra of the *o*-, *m*-, and *p*-chlorophenylpyrazolones prepared are quite similar in their characteristics. In neutral solution these pyrazolones exhibit two maxima, one of high intensity at short wavelength and one of low intensity at longer wavelength. These results indicate that during the spectra determination in alcoholic solution the pyrazolones existed in at least two tautomeric forms; one with a carbon nitrogen double bond, formula I or II, and the other with the carbon carbon double bond as shown in formulas II and III.

Infrared Absorption Spectra

The infrared absorption spectra of the pyrazolones were determined with a Perkin-Elmer spectrometer. The results obtained are given in Tables IV, V, and VI and some data are plotted in Figs. 4, 5, and 6.

Because of the three tautomeric structures theoretically possible for the 1,3,4-trisubstituted pyrazolones, they may be expected to give rise to very complicated infrared spectra. The problem of interpretation of those spectra

TABLE IV

INFRARED ABSORPTION MAXIMA OF 1-*o*-CHLOROPHENYL-3-PHENYL-4-MONOALKYL-5-PYRAZOLONES

R	Absorption bands, cm.$^{-1}$					
H	1640	1565	1515	1345	1260	1165
CH_3	1645	1575	1535	1315	1265	1120
C_2H_5	1630	1580		1310	1255	1120
C_3H_7	1635	1590	1570	1315	1230	1115
C_4H_9	1630	1575		1325	1250	1125
C_5H_{11}	1640	1610	1580	1310	1250	1120
C_6H_{13}	1630	1575		1315	1240	1170
C_7H_{15}	1640	1610	1575	1325	1255	1125
C_8H_{17}	1640	1615	1580	1315	1250	1125
C_9H_{19}	1640	1610	1585	1320	1250	1120
$C_6H_5CH_2$	1630	1575	1310	1255	1215	1110

TABLE V

INFRARED ABSORPTION MAXIMA OF 1-*m*-CHLOROPHENYL-3-PHENYL-4-MONOALKYL-5-PYRAZOLONES

R	Absorption bands, cm.$^{-1}$					
H	1710	1590	1490	1320	1290	1120
CH_3	1650	1590	1500	1325	1245	
C_2H_5	1650	1590	1480	1330	1230	1120
C_3H_7	1640	1585	1480	1315	1230	1125
C_4H_9	1660	1590	1480	1310	1210	1120
C_5H_{11}	1700	1590	1500	1300		1130
C_6H_{13}	1675	1575	1420	1375	1230	1120
C_7H_{15}	1680	1580	1420	1320	1250	1125
C_8H_{17}	1640	1580	1415	1325	1250	1120
C_9H_{19}	1640	1580	1420	1320	1250	1120
$C_6H_5CH_2$	1640	1575	1490	1310	1230	1110

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TABLE VI

INFRARED ABSORPTION MAXIMA OF
1-*p*-CHLOROPHENYL-3-PHENYL-4-MONOALKYL-5-PYRAZOLONES

R	Absorption bands, cm.$^{-1}$					
H	1700	1590	1432	1332	1177	1120
CH_3	1660	1590	1485	1330	1183	
C_2H_5	1700	1605	1562	1490	1162	1090
C_3H_7	1695	1580	1484	1320	1160	1130
C_4H_9	1630	1575	1410	1310	1212	1115
C_5H_{11}	1710	1590	1492	1320	1185	1100
C_6H_{13}	1640	1570		1310	1175	1120
C_7H_{15}	1650	1575		1315	1180	1115
C_8H_{17}	1660	1580	1410	1310	1250	1120
C_9H_{19}	1635	1580	1405	1318	1250	1120
$C_6H_5CH_2$	1640	1575		1310	1250	1105

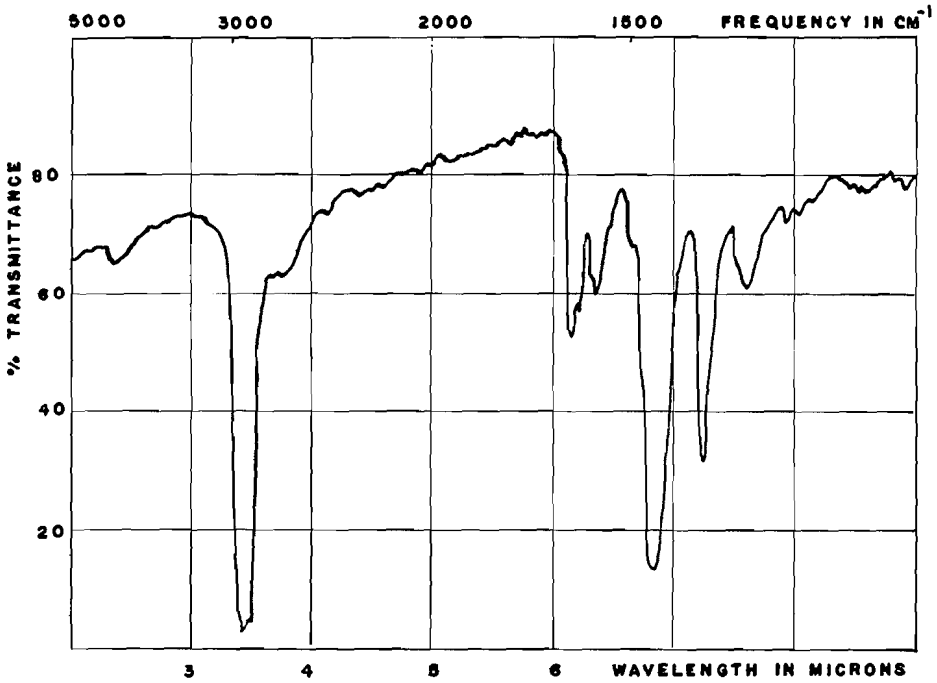

FIG. 4. Infrared absorption spectrum of 1-*o*-chlorophenyl-3-phenyl-4-methyl-5-pyrazolone.

is difficult since few reference spectra for pyrazolones are available in the literature. The absorption spectrum of the 3-methyl-5-pyrazolone has been reported by Randall and his co-workers (10) and he only gave an assignment for a cyclic C=N band. The infrared spectra of several 4-monosubstituted-1,3-diphenyl-5-pyrazolones were determined by Gagnon, Boivin, and Paquin (6). Bond assignments were made tentatively for the C=O group at 1700 cm.$^{-1}$ and the C=N group at 1600 cm.$^{-1}$. Gagnon, Boivin, MacDonald, and Yaffe (5) have studied the absorption spectra of 2-substituted-3-hydroxy-5-pyrazolones and assigned a band in the region of 3300 cm.$^{-1}$ to an OH group. The presence of

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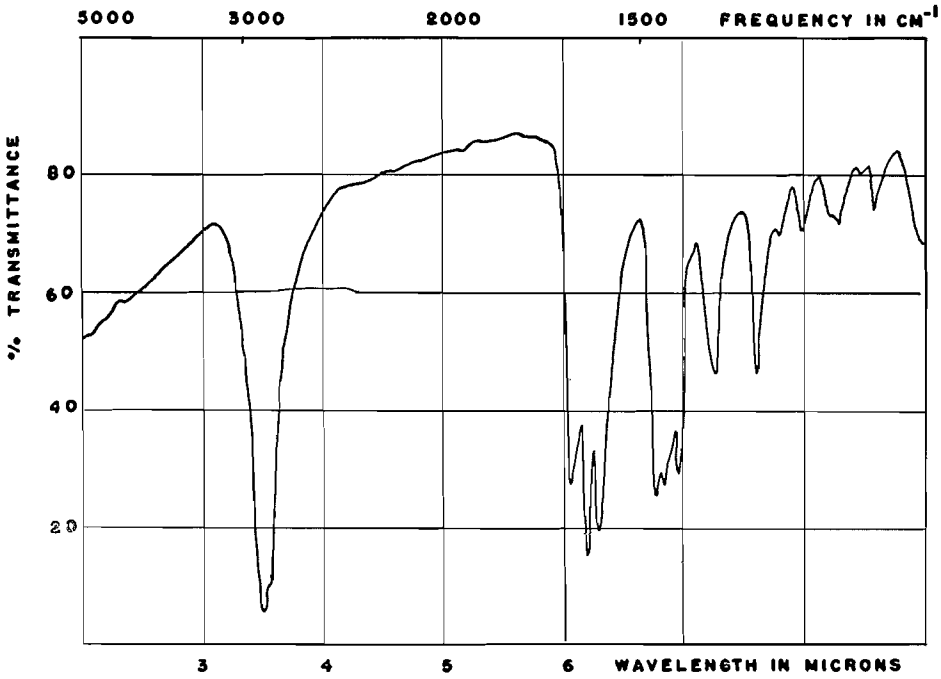

FIG. 5. Infrared absorption spectrum of 1-*m*-chlorophenyl-3-phenyl-4-butyl-5-pyrazolone.

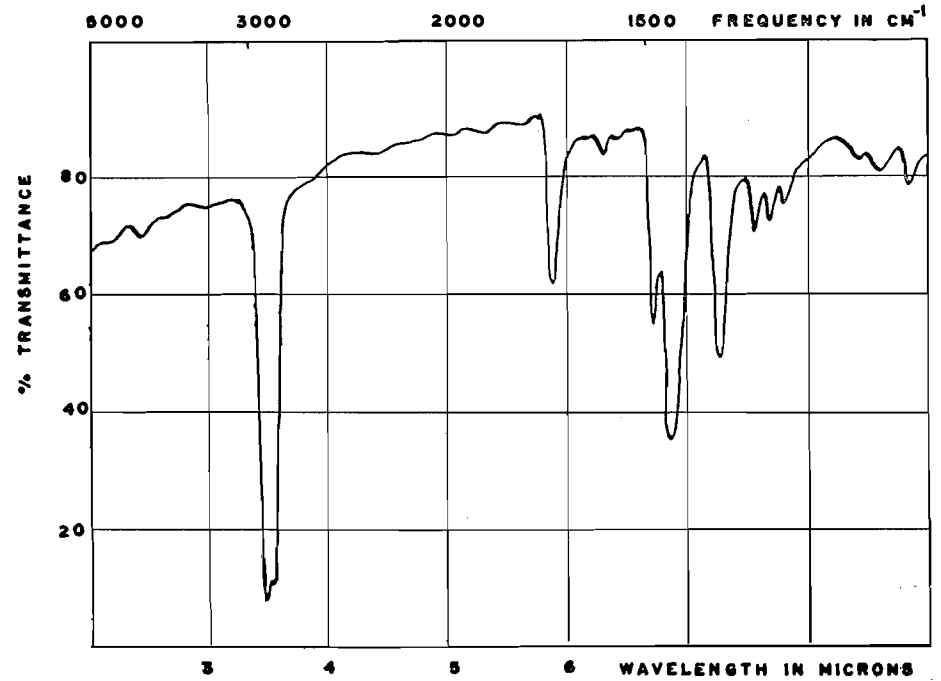

FIG. 6. Infrared absorption spectrum of 1-*p*-chlorophenyl-3-phenyl-4-propyl-5-pyrazolone.

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that group was also proved by chemical methods. Another band occurring in the region of 1670–1700 cm.$^{-1}$ was attributed to a C=O group. A third band in the region of 1590–1680 was attributed to a C=N band as suggested by Randall (10) after studying many cyclic nitrogen compounds such as thiazolidines, imidazolines, and pyridines.

In the present investigation band assignments can be made for two functional groups. An absorption band of high intensity occurring in the region of 1630–1710 cm.$^{-1}$ is attributed to a C=O group. Randall and his co-workers have assigned an absorption band in this region to the carbonyl group for the lactams; therefore it is reasonable to do the same for pyrazolones. Furthermore the absence of a band in the region of 3300 cm.$^{-1}$ characteristic of an OH group is another proof for the presence of a carbonyl group.

A second band occurs in the double band region and absorbs in the range of 1565–1610 cm.$^{-1}$. This band is attributed to a C=N group as suggested by Randall after having studied many cyclic nitrogen compounds.

From those results, one might conclude that in the solid state the pyrazolones prepared have the form CH—C=N while in alcoholic solution this form is in equilibrium with its tautomer C=C—NH.

EXPERIMENTAL PART*

1-o-Chlorophenyl-3-phenyl-4-alkyl-5-pyrazolones

A mixture of ethyl-α-monosubstituted-α-benzoylacetate (0.02 mole) and *o*-chlorophenylhydrazine hydrochloride (0.02 mole) was heated under reduced pressure for three hours at 110–120° C. The red viscous liquid obtained was cooled and dissolved in sodium hydroxide (5%, 200 ml.). The solution was filtered and washed with ether until the extracts were no longer colored. The alkaline solution was cooled and acidified with acetic acid (50%). The precipitate obtained was recrystallized from alcohol or petroleum ether. The pyrazolones are listed together with their melting points, analyses, and ultraviolet absorption spectra in Table I and the infrared data are given in Table IV. Typical ultraviolet absorption curves are plotted in Fig. 1 while some infrared data are plotted in Fig. 4.

1-m-Chlorophenyl- and 1-p-Chlorophenyl-3-phenyl-4-monosubstituted-5-pyrazolones

A mixture of ethyl-α-monosubstituted-α-benzoylacetate (0.02 mole) and *m*-chlorophenyl- or *p*-chlorophenyl-hydrazine was heated under reduced pressure for three hours at 110–120° C. and then for one hour at 170–180° C. The red viscous liquid was treated in a manner similar to that used to obtain the 1-*o*-chlorophenylpyrazolones. The melting points, analyses, and ultraviolet absorption maxima are given in Tables II and III. The infrared absorption bands are given in Tables V and VI and some data are plotted in Figs. 5 and 6.

Preparation of Ethyl Benzoylacetate-α-C^{14}

Magnesium (5.6 gm., 0.23 mole) was placed in a flask equipped with a condenser and a mechanical stirrer. Ethyl malonate (32 gm., 0.20 mole) and

**All melting points are uncorrected.*

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ethyl malonate-2-C^{14} (10 mgm. containing 0.1 mc. of activity) were added. The reaction was initiated with a few drops of carbon tetrachloride and when it subsided, dried ether (75 ml.) was introduced. After all the magnesium had reacted, benzoyl chloride (31 gm., 0.22 mole) was added dropwise while the mixture was refluxed and stirred. When the reaction was completed the solution was cooled and diluted with water (100 ml.). The compound $C_6H_5COCH(CO_2C_2H_5)_2.3H_2O$ crystallized from ether. That substance was decomposed with dilute sulphuric acid. The product was extracted with ether, dried, and distilled. B.p.: 185–190° C. at 12 mm. The benzoyl malonate-2-C^{14} was decarboxylated by steam distillation in dilute sulphuric acid solution. The distillate was neutralized with sodium bicarbonate, extracted with ether, dried, and distilled. B.p.: 113–116° C. at 2 mm.

1-o-Chlorophenyl-3-phenyl-5-pyrazolone-4-C^{14}

Ethyl benzoylacetate-α-C^{14} (3.84 gm., 0.02 mole) was heated with *o*-chlorophenylhydrazine hydrochloride (3.58 gm., 0.02 mole) during three hours at 110–120° C. The product of the reaction was dissolved in sodium hydroxide solution and purified by several extractions with ethyl ether. Acidification with acetic acid (50%) gave the labelled pyrazolone, which was crystallized from ethyl alcohol. Yield, 3.3 gm., 61%.

1-m-Chlorophenyl- and 1-p-Chlorophenyl-3-phenyl-5-pyrazolones-4-C^{14}

A mixture of ethyl benzoylacetate-α-C^{14} (1.92 gm., 0.01 mole) and *m*-chlorophenyl- or *p*-chlorophenyl-hydrazine (1.43 gm., 0.01 mole) was heated under reduced pressure for three hours at 110–120° C. and then for one hour at 170–180° C. The product obtained was treated in a manner similar to that used to obtain the 1-*o*-chlorophenylpyrazolone. The chemical yields varied from 60 to 70%, after purification from ethyl alcohol.

Combustion of C^{14} Products, Plating, and Counting

Samples weighing about fifteen milligrams were completely transformed into carbon dioxide by burning them in a closed system in the presence of oxygen. The carbon dioxide evolved was absorbed in two traps containing carbonate-free sodium hydroxide. After some ammonium chloride was added, the carbonate was precipitated with barium chloride. The barium carbonate was transferred to an aluminum counting plate by centrifuging. Sufficient barium carbonate was added to each plate to ensure "infinite thickness". When dry, the samples were counted using an end window Geiger-Müller counter. The results obtained are given in Table VII.

TABLE VII

COUNTING DATA OF 1-CHLOROPHENYL-3-PHENYL-5-PYRAZOLONES-4-C^{14}

1-Chloro	Weight, mgm.	Total count	Time, min.	Thickness, mgm./cm.^{2}	Net activity, c./min.
Ortho	13.1	20758	25	30.4	801
Meta	13.6	23082	25	30.8	894
Para	13.9	21896	25	31.0	847

Ultraviolet Absorption Spectra

The ultraviolet absorption spectra of the pyrazolones were taken on a Beckman Spectrophotometer Model DU. The method has been previously described (4). The solvent used was ethanol (95%). The results are listed in Tables I, II, and III and some of the data are plotted in Figs. 1, 2, and 3.

Infrared Absorption Spectra

All the infrared absorption spectra of the pyrazolones were obtained with a Perkin-Elmer Model 21 double-beam null principle recording spectrophotometer. The method has been described in the literature (6). The spectra covering the range 5000–1100 cm.$^{-1}$ only are given in Figs. 4, 5, and 6. The curves all show the four specific bands of nujol. The other absorption bands are listed in Tables IV, V, and VI, and have been discussed in the theoretical part.

ACKNOWLEDGMENTS

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REACTION OF ALDOSES AND KETOSES WITH LEAD TETRAACETATE[1]

By A. S. Perlin and Carol Brice

ABSTRACT

Lead tetraacetate is highly selective for oxidation of α-hydroxy-hemiacetal groups and hence most readily attacks cyclic forms of the sugars. The reaction proceeds stepwise; the hemiacetal α-glycol being cleaved and the monoester of a correspondingly shorter-chained sugar formed. After cyclization the new sugar in turn is oxidized at the hemiacetal α-glycol group to yield a diester of a still-lower-order member of the series. In this manner D-glucose first yields mono-*O*-formyl-D-arabinose and then di-*O*-formyl-D-erythrose. Similarly, D-fructose is degraded to a glycolate ester of D-erythrose and finally to a formate–glycolate diester of D-glyceraldehyde. Some relatively rare sugars thus may conveniently be prepared directly from abundant higher-order members of the series. The reactions appear to involve preferential attack of the furanose form of a sugar rather than of the normally-predominant pyranose form, or possibly migration of ester groups towards the reducing end of the sugars.

Criegee noted that D-glucose rapidly consumes about three moles of lead tetraacetate in warm acetic acid without concurrent production of formaldehyde (5). He suggested that the apparent failure of the oxidant to attack the 5,6-glycol group was due to the presence of the 1,5-hemiacetal oxygen bridge, and that the sugar must therefore be oxidized as a ring, rather than in the open-chain form. According to Hockett and Zief (14) D-glucose at 20°C. quickly consumes only two moles of lead tetraacetate and further oxidation is very slow. If the sugar exists in solution predominantly as D-glucopyranose (I) it would be expected to consume at least three moles of oxidant, as had been found by Criegee, and possibly yield 2-*O*-formyl-D-glyceraldehyde (II). For the related oxidant, periodic acid, this possibility has been verified recently by Schöpf and Wild (28) who isolated D-glyceraldehyde monoformate by treating D-glucose with a limited quantity of periodate. In contrast to these results, Abraham (1) reported that D-glucose in warm aqueous acetic acid is completely but slowly degraded by lead tetraacetate to five moles of formic acid and one mole of formaldehyde, the reaction being recommended for radioactive-carbon assay. Hence the literature records at least three different sets of data for the reaction of D-glucose with lead tetraacetate. These variations are attributable most probably to the differences in the oxidation conditions employed but they invited further examination of the reaction.

The results of Hockett and Zief were of particular interest since the consumption of only two moles of oxidant would be expected to afford a derivative of a tetrose, rather than of a triose. Accordingly, D-glucose, in glacial acetic acid or in acetic acid containing 1–2% of water (2), was treated at room temperature with excess lead tetraacetate. Two moles of oxidant were consumed within three minutes and oxidation proceeded subsequently at a

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markedly slower rate reaching a value of 2.1 moles in one hour; the rapidity of the reaction may be contrasted with the relatively slow oxidation rates of polyols (12) and glycosides (13). The product of the initial rapid oxidation, isolated as a sirup in 95% yield, was strongly reducing, very soluble in ethyl acetate, and it absorbed strongly in the infrared region at about 1170 cm.$^{-1}$, characteristic of formate esters (31). In agreement with the latter result two moles of formic acid were liberated when the compound was hydrolyzed with acid or alkali. Acid hydrolysis afforded D-erythrose as the sole sugar (23), characterized by hydrogenation to give erythritol, by oxidation to give D-erythrono-γ-lactone, by formation of a 2,5-dichlorophenylhydrazone, and by comparison of its specific rotation, infrared absorption spectrum, and paper chromatographic behavior with those of authentic D-erythrose. The product of the oxidation of D-glucose with lead tetraacetate is therefore a diformate ester of D-erythrose.

The position of the formate substituents has not been definitely established, in part because of the groups' high instability. For example, formic acid is released spontaneously when the compound is dissolved in water, and the ester groups are removed when the compound is hydrogenated in alcohol at room temperature with platinum oxide (23). This instability thus adds to the difficulty so often encountered in attempting to determine the position of acyl substituents. Because the compound is so very slowly oxidized by lead tetra-

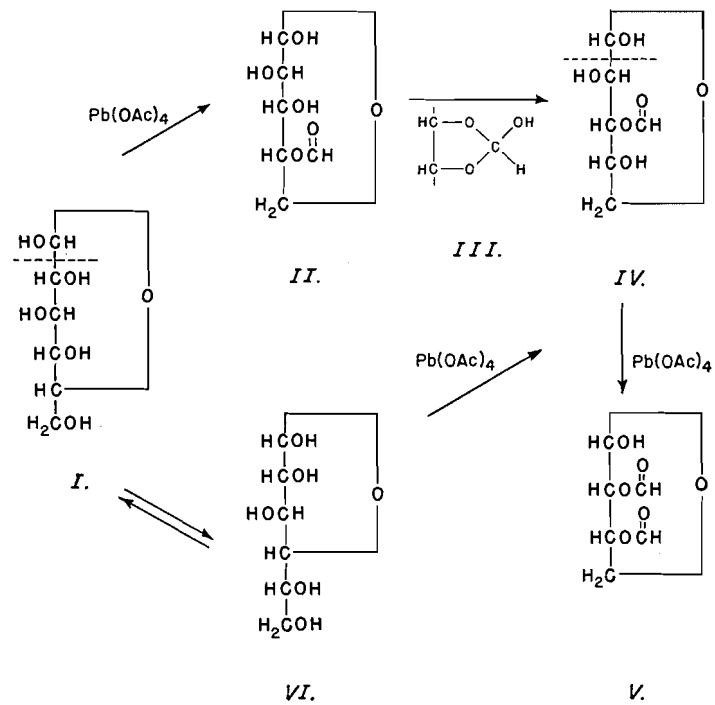

FIG. 1. Oxidative degradation of D-glucose to di-*O*-formyl-D-erythrose.

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acetate one formate group is most likely at the 2-position; the second ester group, however, could be on either carbon 3 or 4.

Degradation of D-glucose to a 2,3- or 2,4-diformate ester of D-erythrose may occur in one or both of at least two different ways. According to one of these possibilities (Fig. 1) D-glucopyranose (I) is oxidatively cleaved at the hemiacetal α-glycol group to yield 4-*O*-formyl-D-arabinose (II). Acyl-migration of the formate group to the 3-position (IV) then takes place, perhaps via the orthoacid (III). The newly-formed hemiacetal α-glycol of the pentose consumes a second mole of oxidant to yield 2,4-di-*O*-formyl-D-erythrose, or, if a second acyl-migration follows to permit ring closure, 2,3-di-*O*-formyl-D-erythrose (V). Several known instances of acyl-migration (see 30) provide precedence for this suggested route. However, little is known of the behavior of formate groups because very few sugar formates have been prepared and characterized. The great rapidity of the oxidation as compared with the rates of reaction of, for example, polyols or glycosides may be accommodated by this route if the oxidation proceeds by an ionic mechanism (4, 18) since the hemiacetal α-glycol would be the prime site of carbonium-ion formation.

An alternative route could be depicted by assuming that α-D-glucofuranose (VI), although present perhaps in small proportion, is oxidized preferentially. Thus oxidation of the α-hydroxy-hemiacetal group, accompanied by displacement of the pyranose–furanose equilibrium, would yield 3-*O*-formyl-D-arabinose (IV) directly, which as a furanose sugar in turn would be degraded to (V). The possibility that the furanoid form of the sugar is oxidized preferentially finds support in the fact that the five-membered furan ring is nearly planar and the hemiacetal α-glycol group of α-D-glucofuranose is therefore more nearly able to assume a true *cis* (0°) position. Reeves (26) has shown that compounds having true *cis*-α-glycols, such as 2,3-dihydroxy tetrahydrofuran, react extremely rapidly with lead tetraacetate and may, in fact, be titrated with the reagent in the presence of ethylene glycol or methyl glycopyranosides containing a *cis*-α-glycol group. He noted, further, that reducing sugars can interfere with the titration since they presumably may form furanose rings containing true *cis*-α-glycol groups. The lead tetraacetate – glycol reaction possesses second order kinetics (6, 25) and therefore should require a relatively high concentration of the furanose modification to account for the observed rate of oxidation of D-glucose. However, the position of the pyranose–furanose equilibrium in acetic acid solution is not known, but the great rapidity of the interconversion between the two forms (17) might be sufficient to accommodate displacement of the equilibrium in favor of the latter as oxidation proceeds. This may be true particularly for acetic acid, in which mutarotation is extremely rapid. Thus, it was not possible to observe the changes in rotation when α- or β-D-glucose, dissolved quickly in a minimum quantity of water, was taken up in acetic acid; the specific rotation in each solution had reached an equilibrium value of $[\alpha]_D$ +70° before the polarimeter reading could be made.

From Reeves' data (26) it may be inferred that reducing sugars are titratable in the presence of substances such as ethylene glycol. If, then, α-D-gluco-

furanose is the species oxidized, the hemiacetal α-glycol should be preferred as the point of attack rather than the 5,6-glycol group. Once D-arabinose formate is produced the new hemiacetal ring, either pyranose or furanose, could in turn prevent oxidation of the terminal glycol group. The failure of methyl α-D-mannofuranoside to yield formaldehyde when oxidized with lead tetraacetate was explained in a similar manner (5). On the other hand, absence of oxidation at the 5,6-glycol group of D-glucose could be regarded as evidence favoring the interpretation that D-glucopyranose is the form involved in the reaction, with the hemiacetal ring at carbon-5 preventing attack.

Considering these possibilities further the oxidation behavior of D-*glycero*-D-*gulo*heptose and D-*erythro*-D-*gala*octose was examined. Even in the pyranose form the heptose contains a free terminal 1,2-glycol group and the octose, a 1,2,3-triol group. Thus if a pyranose ring in glucose is required to explain the results just discussed, cleavage of the terminal groups of the higher sugars would be expected. Like D-glucose, the heptose and octose also rapidly consumed two moles of lead tetraacetate and a relatively slow reaction then followed (Fig. 2). When two moles of oxidant had been consumed by the heptose, arabinose was the only product detected chromatographically and the amount (colorimetrically determined) was one mole per mole of heptose. These results corresponded to quantitative removal of carbon atoms 1 and 2 without simultaneous attack at carbons 6 and 7. In 24 hr. reaction time the consumption of oxidant had increased to 3.4 moles per mole but arabinose was still the only product detectable on the chromatogram and the quantity present was now 0.65 moles per mole. The 0.35 moles of pentose formate which appeared to have been completely oxidized in the interim accounted for the extra 1.4 moles of oxidant consumed (i.e., 4 moles per mole of pentose $\times 0.35$). Similarly, the octose yielded the expected glucose on oxidation with two moles of lead tetraacetate and glucose was still present when consumption of oxidant reached four moles per mole. Therefore, it was evident that the terminal glycol groups did not require protection from the original pyranose ring in order to escape oxidation, and the reactions could be depicted in the same general manner as already indicated for D-glucose (Fig. 1). Accordingly the product from the heptose would be 2,3- or 2,4-di-*O*-formyl-D-arabinose and from the octose, 2,3- or 2,4-di-*O*-formyl-D-glucose and further oxidation could result from ring opening and slow hydrolysis of ester groups followed by complete oxidation of the compounds.

In addition to D-glucose other aldoses also rapidly consume two moles of lead tetraacetate (Fig. 3), although a further relatively fast oxidation occurs with some of the compounds. The reaction rates illustrated in Fig. 3 have been greatly reduced relative to those in Fig. 2 by employing a reaction temperature of 0°C. in a mixture of acetic and propionic acids, so that the early portion of the reaction could be examined; the consumption of oxidant by each sugar at room temperature in acetic acid reaches approximately the same level as at the lower temperature. In no instance is a consumption of three moles, expected of a pyranose sugar, attained. Moreover, there is a wide diversity in

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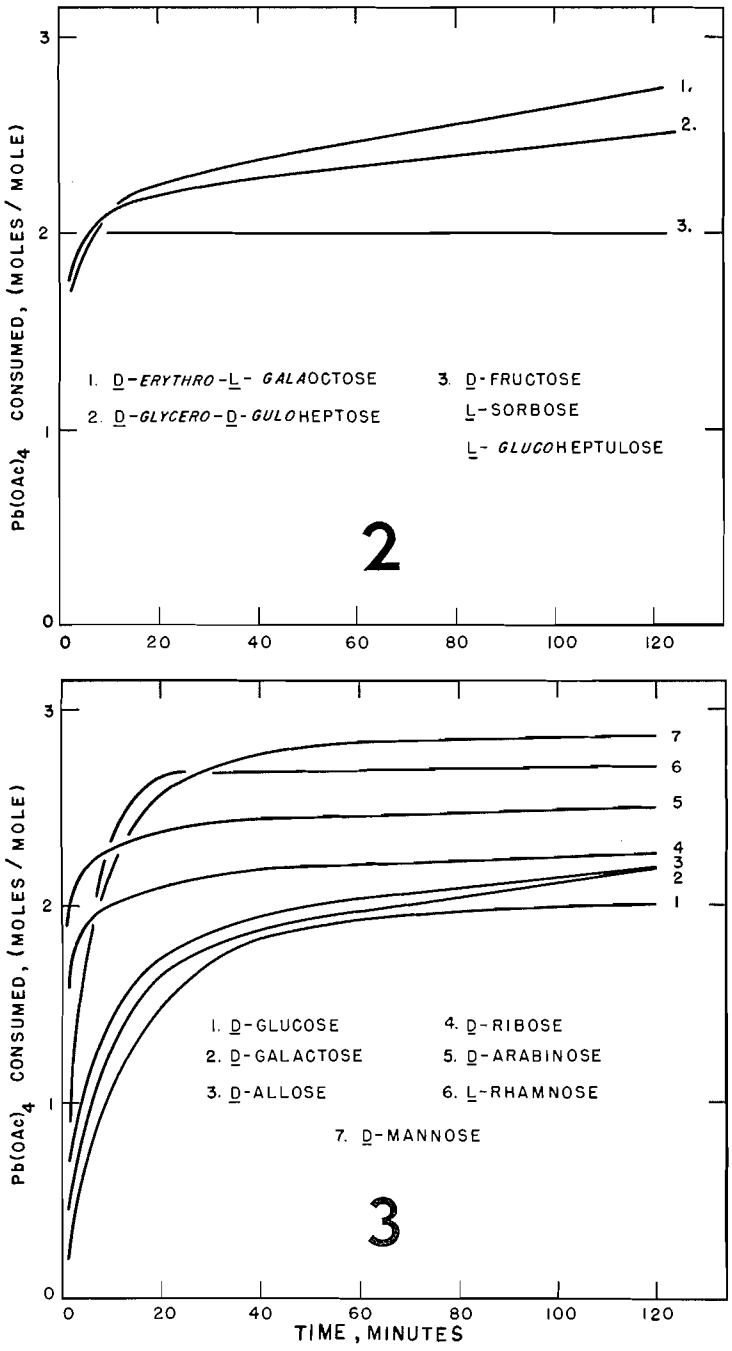

FIG. 2. Rates of lead tetraacetate consumption at room temperature (*ca.* 25°C.).

FIG. 3. Rates of lead tetraacetate consumption for aldoses at 0°C.

the rates of oxidation. These differences have shown no obvious correlation with structural differences between the compounds nor with the predicted stabilities from Reeves' measurements of fixed pyranose rings of the sugar glycosides (27).

Despite these variations the oxidations in general appear to follow a pattern similar to that already described for D-glucose with departures occurring in differing degree. For example, the oxidation of L-arabinose with two moles of lead tetraacetate affords a 90% yield of a sirupy product which from analysis appears to be a triose containing approximately 1.5 formate ester groups, and which on hydrolysis gives L-glyceraldehyde (23), characterized as the dimedon derivative. This triose formate again indicates a cleavage of carbon atoms 1 and 2 from the reducing end of the parent aldose and its production, in part, may be described by the same type of reaction sequences as presented above. The oxidation of D-galactose even more closely resembles the reaction with D-glucose. Treatment with two moles of lead tetraacetate gives a product which contains approximately 1.8 ester groups and which on hydrolysis yields D-threose, characterized as tri-*O*-acetyl-α-D-threose, by hydrogenation to D-threitol, and as a 2,5-dichlorophenylhydrazone. The specific rotation of the D-threose is about $[\alpha]$ $-12°$, which is also the value assigned by Hockett and co-workers (10, 11), who prepared the compound by other methods, but different from Freudenberg's value of $+19°$ (7). By consuming 2.7 moles of lead tetraacetate, D-mannose appears to differ most markedly from D-glucose. It will be seen, however, that in some respects the oxidations of these two compounds are closely similar.

To account for the conversion of a hexose to a tetrose containing two formate ester groups it has been necessary to assume that the oxidation proceeds *via* a pentose monoformate. It was expected therefore that on treatment with somewhat less than two moles of lead tetraacetate a hexose should yield the related pentose, which would constitute a new procedure for the stepwise shortening of the carbon chain of sugars. Accordingly, when D-glucose-1-C^{14} was oxidized with one mole of lead tetraacetate (21) the products found on paper chromatograms after precipitation of lead as the oxalate were unoxidized D-glucose (radioactive by radioautography), a compound which gave color tests for pentoses but which travelled more rapidly than the pentoses (radioactive), and a third compound which travelled at a rate similar to that of D-erythrose diformate (radioactive). After acid hydrolysis to remove ester groups the latter two compounds were no longer radioactive and travelled on the paper chromatogram at the same rate as arabinose and erythrose, respectively. The pentose, subsequently isolated and characterized as D-arabinose, was undoubtedly therefore the expected monoformate ester but the yield was only about 15%. Possibly this low yield is obtained because D-arabinose is much more rapidly oxidized than is D-glucose (Fig. 3) and hence is converted to D-erythrose instead of being accumulated. Application of this reaction to studies employing C^{14}-labelled sugars has been suggested (21).

D-Mannose is oxidized much more rapidly than glucose and since, like D-glucose, it also is degraded to D-arabinose the amount of the pentose oxidized

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further to D-erythrose is proportionately less (Fig. 2). When treated with 0.8 moles of lead tetraacetate, for example, D-mannose gave D-arabinose in about 35% yield; since 35% of the D-mannose remained unoxidized the actual conversion of hexose to pentose was greater than 50%. A 35% yield of pentose was also obtained in the degradation of D-galactose to D-lyxose. On oxidation with one mole of lead tetraacetate D-altrose and D-allose are degraded to D-ribose, the yields being approximately 70% and 20%, respectively. The difference between these two hexose epimers appears again to be related to differences in oxidation rates; D-altrose consumes lead tetraacetate at a rate close to that of D-mannose, attaining an oxidation level of 2.6 moles per mole, but D-allose is oxidized much more slowly (Fig. 3). These results support the suggestion that the lead tetraacetate reaction involves an initial attack at the α-hydroxy-hemiacetal group, but also indicate that the conformation of the rest of the molecule markedly affects the rate of oxidation.

According to Hockett and co-workers (14, 13) D-fructose also consumes only two moles of lead tetraacetate and at a rate close to that for D-glucose. In the present investigation this result was confirmed and similar results were also obtained with L-sorbose and L-*gluco*heptulose (Fig. 3). The product from the oxidation of D-fructose with two moles of lead tetraacetate, isolated in 95% yield, gave on hydrolysis approximately one mole each of formic acid, glycolic acid, and D-glyceraldehyde (24). Similarly, the oxidation of L-sorbose produced a formic acid – glycolic acid diester of L-glyceraldehyde (24). The formation of these diesters from ketohexoses may be described by reaction sequences (Fig. 4) similar to those considered earlier for aldose oxidations. Assuming β-D-fructofuranose (VII) to be the species chiefly concerned in the

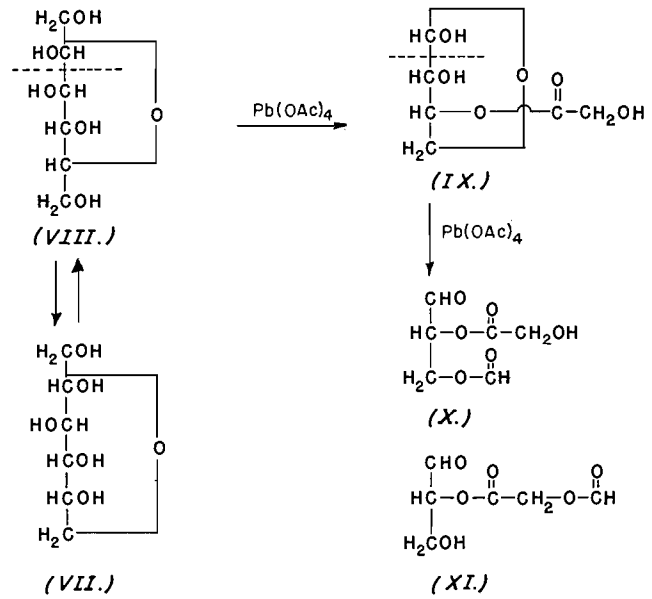

FIG. 4. Oxidative degradation of D-fructose to a formate–glycolate diester of D-glyceraldehyde.

reaction, the initial attack cleaves the hemiacetal α-glycol group to yield 3-*O*-glycolyl-D-erythrose (VIII), which in turn is degraded to 3-*O*-formyl-2-*O*-glycolyl-D-glyceraldehyde (IX). Alternatively compounds VIII and IX may be produced from D-fructopyranose by an initial acyl-migration of the glycolic acid ester group from carbon atom 4 of D-erythrose to carbon atom 3. Since the glycolate ester group itself contains a primary hydroxyl the latter conceivably could also accommodate the formate ester group, as in X.

A mechanism for the reaction of aldoses and ketoses with lead tetraacetate cannot be described at present with certainty. It is seen, however, that the oxidation is highly selective for α-hydroxy-hemiacetal groups, and hence involves cyclic forms of the sugars almost exclusively as first proposed by Criegee (5). The reaction proceeds stepwise with cleavage of the hemiacetal α-glycol group and formation of a monoester of a new sugar having a shorter carbon-chain. After cyclization the new sugar in turn is attacked oxidatively at the hemiacetal α-glycol group to yield a diester of a still-lower-order member. No racemization appears to be involved in these reactions. With aldoses the oxidation tends to stop after the consecutive scission of carbons 1 and 2, and to yield a diformate ester of the corresponding sugar with two carbon atoms less. The initial oxidation of ketoses involves cleavage of carbons 1 and 2 together as glycolic acid and the reaction then stops after carbon 3 is converted to formic acid, the final product being a formate–glycolate diester of the corresponding sugar having three carbon atoms less. Because of these characteristics the reaction constitutes a means for the stepwise degradation of sugars and thus provides a simple method for preparing some relatively rare carbohydrates directly from higher-order members of the series.

EXPERIMENTAL

Lead tetraacetate was prepared according to the procedure recommended by Vogel (32), or was obtained commercially (Matheson Co., Inc.), and was kept moist with acetic acid during storage. The weight taken for a reaction was based on the predetermined oxidant content of the wet material. If the lead tetraacetate was dark it was recrystallized from acetic acid before use, or it was dissolved in acetic acid and the solution was filtered and added directly to the aqueous acetic acid solution of the sugar.

Cellulose chromatography was carried out according to Hough *et al.* (16) using butanol, half-saturated with water, as the developing solvent. The eluate was first passed through a Seitz bacterial filter and after distillation of the solvent the sugar sirup was extracted with water and clarified with charcoal.

Pentose was estimated colorimetrically by the orcinol method (20). The lead was precipitated with excess oxalic acid, the acetic acid was distilled, and the residue was taken up in water and its pentose content estimated. The values obtained were not corrected for possible interference by other sugars present.

Solutions were concentrated *in vacuo* at 35–40°C.

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Measurement of Oxidation Rates

Measurements were made both at room temperature (about 25°C.) and at 0°C. In experiments carried out at room temperature the sugar (25–30 mgm.), dissolved in 0.4 ml. of water (2), was taken up in 20 ml. of acetic acid. At zero reaction time 400 mgm. of lead tetraacetate in 20 ml. of acetic acid was added to the sugar solution, a reagent blank being run simultaneously. Five-milliliter aliquots of the reaction mixture were withdrawn at desired intervals and treated with 10 ml. of stopping solution (10 gm. of potassium iodide and 50 gm. of sodium acetate in 100 ml. of water (4)), and the iodine released was titrated with sodium thiosulphate. Some reactions were carried out in glacial acetic acid, the sugar being first finely ground and dissolved directly.

*Di-O-formyl-*D*-erythrose*

D-Glucose (1.5 gm., 8.3 mM.) dissolved in 3 ml. of water was taken up in 150 ml. of acetic acid. Lead tetraacetate (7.7 gm., 17.4 mM.) was added to the rapidly stirred sugar solution over a period of three to four minutes. When the oxidant had dissolved, oxalic acid dihydrate (1.9 gm.) dissolved in acetic acid was added, and the suspension was stirred for an additional 30 min. The precipitate was filtered and washed with acetic acid and the filtrate was concentrated to a volume of a few milliliters. Ethyl acetate was added and the precipitate which formed was triturated with several portions of ethyl acetate. The extracts were combined, filtered, and concentrated to a sirup which was further purified twice by extraction into ethyl acetate. The product (1.3 gm.) was a clear, pale yellow oil, $[\alpha]_D^{25}$ +20° (*c*, 3, water) dropping slowly owing to hydrolysis of the ester groups. The infrared absorption spectrum showed very strong absorption at 1725 cm.$^{-1}$ and at 1170 cm.$^{-1}$, characteristic of formate esters (31). A sample of the oil (7.4 mgm.) required 8.35 ml. of 0.010 *N* sodium hydroxide in 10 min. reaction time at room temperature, equivalent to 2.0 formate ester groups per mole. Another sample (21.5 mgm.) was slowly titrated with 0.05 *N* sodium hydroxide to a phenolphthalein end point. The solution was then acidified with sulphuric acid and extracted continuously with ether for four hours; the ether extract required 5.20 ml. of 0.048 *N* sodium hydroxide, equivalent to 2.0 formate ester groups per mole. The formic acid content of the ether extract was determined by lead tetraacetate – potassium acetate titration (22) to be equivalent to 2.0 moles per mole. On hydrolysis with dilute acid the compound gave D-erythrose in 90% yield (23).

One sample of the ester which had been kept at 3°C. for several months partially crystallized but the crystalline material could not adequately be separated from the sirup. The infrared absorption spectrum of a specimen from which the majority of sirup had been separated by tiling was similar to that of the sirup but the absorption bands were sharper and now appeared as doublets. The crystalline material failed to induce crystallization of other preparations of the diester and may possibly have been a monoester formed by slow hydrolysis during storage.

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D-*Threose Formate Ester*

D-Galactose was treated with 2.05 molar equivalents of lead tetraacetate and the reaction mixture was worked up as described above for the preparation of di-*O*-formyl-D-erythrose; 1.5 gm. of D-galactose yielded 1.2 gm. of sirup, $[\alpha]_D^{27}$ +15° (*c*, 3, water) dropping slowly owing to hydrolysis of the ester groups. Alkaline hydrolysis indicated that the compound contained 1.8 formate groups per mole. The infrared absorption spectrum was very similar to that of D-erythrose diformate.

D-*Threose*

Crude D-threose formate, obtained by distillation of the acetic acid but without purification by extraction into ethyl acetate, was taken up in 0.05 *N* sulphuric acid and heated at 45°C. for 18 hr. to hydrolyze the ester groups. The hydrolyzate was neutralized with Dowex-1 resin (bicarbonate form) and was concentrated to a sirup. Weight, 1.68 gm. from 3.0 gm. of D-galactose. Chromatographic examination with the methyl ethyl ketone solvent (3) showed a major component which travelled slightly faster than D-erythrose, and which gave a yellow-brown color and a bright fluorescence under ultraviolet light with aniline oxalate spray (15); a small quantity of a pentose which corresponded on the paper to D-lyxose was also present. A portion of the sirup (1.1 gm.) was chromatographed on a cellulose column and the tetrose fraction was recovered. Weight 0.70 gm., $[\alpha]_D^{25}$ −12.9° (*c*, 2.3, water). Hockett (10) reports $[\alpha]_D$ −12° for D-threose.

D-*Threitol*

D-Threose formate ester (0.79 gm.) was dissolved in 15 ml. of water and was carefully saponified with 1 *N* sodium hydroxide. Sodium borohydride (0.20 gm.) dissolved in 10 ml. of water was added. A negative Fehling's test was obtained in 90 min. reaction time and acetic acid was then added to decompose excess borohydride. Cations were removed with Amberlite IR-120 resin and boric acid by repeated distillation of the sirup with methanol. The product was recrystallized from ethanol. Weight 0.27 gm., m.p. 76–83°C. After two further recrystallizations, m.p. 86–88°C.; $[\alpha]_D^{25}$ −10.6° (*c*, 1, ethanol), $[\alpha]_D^{25}$ +4.2° (*c*, 1, water) in agreement with literature values (8). Calculated for $C_4H_{10}O_4$: C, 39.34%; H, 8.25%; found: C, 39.62%; H, 8.15%.

Dibenzylidene D-threitol, m.p. 225–226°C., was prepared from the compound according to Haskins and co-workers (8).

*Tri-O-acetyl-α-*D-*threose*

D-Threose sirup (300 mgm.) was heated at 100°C. for one hour with 15 ml. of acetic anhydride and 0.5 gm. of sodium acetate. The acetic anhydride was distilled *in vacuo*, the residue was extracted with chloroform, and the chloroform extract washed with water. After evaporation of the chloroform the product was recrystallized from alcohol. Weight 115 mgm., m.p. 115–118°C. Two further recrystallizations raised the melting point to 118–120°C., $[\alpha]_D^{25}$ +34.4° (*c*, 2, chloroform). Hockett (10) reports m.p. 117–118°C. and $[\alpha]_D$ +35.5° for D-threose triacetate. Calculated for $C_{10}H_{14}O_7$: C, 48.78%; H, 5.73%; acetyl, 52.4%; found: C, 48.90%; H, 5.69%; acetyl, 52.2%.

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D-*Threose 2,5-Dichlorophenylhydrazone*

D-Threose sirup (0.51 gm.), prepared by concentrating an aliquot of the neutral hydrolyzate described above, was dissolved in 20 ml. of methanol in an evaporating dish. 2,5-Dichlorophenylhydrazine (0.75 gm.) was added and the methanol was rapidly evaporated off on the steam bath (procedure of Mandl and Neuberg (19)). The product was taken up in ether, filtered, and the ether was distilled. The residue was dissolved in ethyl acetate, treated with charcoal, and an equal volume of benzene was added. The product (0.60 gm.) had m.p. 103–106°C. Recrystallized twice, m.p. 108–110°C.; $[\alpha]_D^{25}$ +14.4°. A mixed m.p. with D-erythrose 2,5-dichlorophenylhydrazone (m.p. 110–112°C. (23)) was depressed. Calculated for $C_{10}H_{29}O_3N_2Cl_2$: C, 43.03%; H, 4.33%; found: C, 43.08%; H, 4.28%.

Regeneration of D-*Threose from the Hydrazone*

D-Threose 2,5-dichlorophenylhydrazone was treated with benzaldehyde according to the procedure described by Sowden and Fischer (29). The product had $[\alpha]_D$ +21.2° (*c*, 1.5, water) and in addition to the free sugar appeared to contain a glycoside formed presumably during the reflux with alcoholic benzaldehyde. An aqueous solution of the product was acidified with dilute hydrochloric acid and heated on the steam bath for 5–10 min. which effected a sharp decrease in rotation and an increase in reducing power. D-Threose (91 mgm.) was obtained from 280 mgm. of the hydrazone, $[\alpha]_D^{25}$ −11.4° (*c*, 1.8, water). On the paper chromatogram the regenerated D-threose exactly corresponded to the compound isolated by column chromatography.

L-*Glyceraldehyde Formate Ester*

L-Arabinose was treated with 2.1 molar equivalents of lead tetraacetate and the reaction was worked up as described above for the preparation of di-*O*-formyl-D-erythrose. A clear, yellow oil was obtained, 1.2 gm. from 1.5 gm. of L-arabinose. The infrared absorption spectrum of this compound showed strong absorption characteristic of formate ester groups. On saponification the compound consumed alkali equivalent to approximately 1.5 formate ester groups per mole. Hydrolysis of the ester groups in 60% acetic acid afforded L-glyceraldehyde in 83% yield (23).

D-*Arabinose*

D-Mannose (1.0 gm., 5.56 mM.), dissolved in 2 ml. of water, was taken up in 250 ml. of acetic acid. Lead tetraacetate (2.1 gm., 4.73 mM.) was added to the stirred solution; a negative potassium iodide – starch test was obtained within two minutes reaction time. Oxalic acid dihydrate (0.59 gm. in 6 ml. of acetic acid) was added, stirring was continued for an additional 30 min., and the suspension was filtered. The filtrate was evaporated to a sirup which was chromatographed on a cellulose column. Separation of the arabinose from the unoxidized mannose, sometimes difficult by chromatography, was readily achieved in the present instance because the pentose was present in the mixture as the formate ester. Its rate of travel was thus greatly enhanced and it was completely eluted from the column within 24 hr. A fraction containing the D-erythrose formate ester (0.17 gm.) was eluted just ahead of the pentose

and the unoxidized D-mannose (0.34 gm.) was recovered by prolonged elution. In passage through the column the pentose ester was partially hydrolyzed and the product was therefore a mixture of esterified and free sugar. The ester remaining was hydrolyzed by heating in water for three hours on the boiling-water bath, and the final sirup obtained crystallized completely in one to two days. Weight 0.32 gm. Recrystallized from alcohol the product had m.p. 150–152°C., raised by a second recrystallization to 156.5–157.5°C., undepressed by admixture with authentic D-arabinose (m.p. 157°C.). $[\alpha]_D^{27}$ −102.0°. The X-ray diffraction pattern of the compound was identical with that of D-arabinose.

D-Arabinose was prepared also from D-glucose by partial oxidation as described above for D-mannose. The yield of pentose estimated colorimetrically was about 15%, and the product was isolated by chromatography and characterized as the benzoylhydrazone (9), m.p. 185–186°C. The X-ray diffraction pattern was identical with that of D-arabinose benzoylhydrazone.

D-Lyxose

D-Galactose (1.0 gm., 5.56 mM.) was oxidized with 3.4 gm. (7.68 mM.) of lead tetraacetate and the product was worked up as described above under D-arabinose. Prior to chromatography on the cellulose column the formate ester groups were hydrolyzed by heating an aqueous solution of the oxidation products on the boiling-water bath for three hours. D-Threose (0.31 gm.) was eluted first, and 0.19 gm. of unoxidized D-galactose was recovered from the column following the pentose fraction. The middle fraction (0.37 gm.) crystallized completely when seeded with D-lyxose. Recrystallized from alcohol it had m.p. 113–116°C., and mixed m.p. 114–115°C. with authentic D-lyxose (m.p. 116.5°C.). $[\alpha]_D^{25}$ −13.9° (*c*, 2, water).

On acetylation by refluxing with acetic anhydride and sodium acetate the sugar yielded α-D-lyxose tetraacetate, m.p. 94–96°C., undepressed by admixture with an authentic specimen.

3-O-Formyl-2-O-glycolyl-D-glyceraldehyde

D-Fructose was treated with 2.1 molar equivalents of lead tetraacetate as described above for the preparation of di-*O*-formyl-D-erythrose. The ethyl acetate extract afforded a clear, pale yellow sirup, 1.47 gm. from 1.5 gm. of D-fructose. $[\alpha]_D^{25}$ +5.1° (*c*, 1, water) dropping slowly owing to hydrolysis of the ester groups. The infrared absorption spectrum of the compound was similar to that of the formate esters described above, but the carbonyl bands were broader, presumably owing to the contribution of the glycolate ester group. On complete hydrolysis of the ester groups with dilute acid the product gave D-glyceraldehyde in 90% yield (24).

The hydrolyzate obtained from 0.26 gm. of the diester was neutralized by slow addition of Dowex-1 resin (200–400 mesh; bicarbonate form) to the stirred solution and the resin was filtered off and washed. The resin was then shaken with 20 ml. of 1 *N* sulphuric acid for 90 min., filtered and washed well on the filter, and the acid eluate was concentrated to dryness using a dry ice – acetone trap as condenser. Water was added and the distillation resumed,

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and the procedure was repeated four times. The formic acid content of the distillate was determined by lead tetraacetate – potassium acetate oxidation (22) to be 1.1 mM.; requires 1.5 mM. After distillation of the formic acid the residue was three times extracted under reflux with ether. Concentration of the ether extract gave glycolic acid, 0.083 gm. (1.09 mM.; requires 1.5 mM.), m.p. 67–72°C. Recrystallized from ether m.p. 72–75°C., undepressed by admixture with authentic glycolic acid.

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EFFECT OF COMPLEXING ON THE HOMOGENEOUS CATALYTIC ACTIVATION OF HYDROGEN BY CUPRIC SALTS[1]

By E. Peters[2] and J. Halpern

ABSTRACT

The effects of various organic and inorganic complex-forming reagents on the homogeneous catalytic activation of H_2 by Cu^{++} in aqueous solution have been determined. The catalytic activities of the cupric complexes decrease in the order: butyrate, propionate > acetate > $SO_4^=$ > Cl^- > H_2O (i.e. the uncomplexed Cu^{++} ion) > glycine, ethylenediamine. The mechanism of the activation process is discussed.

INTRODUCTION

Detailed kinetic studies of the homogeneous catalytic activation of molecular hydrogen in aqueous perchlorate (11) and acetate (4, 2, 10) solutions were described earlier. In view of the fact that the catalytic activity of the undissociated cupric acetate complex was found to be about 120 times greater than that of the uncomplexed cupric ion, it seemed of interest to examine the effect of other complexing agents. In the present paper kinetic studies on the catalytic activation of hydrogen by a number of organic and inorganic cupric complexes are described.

EXPERIMENTAL

Glycine and ethylenediamine were Eastman white label grade products. All other chemicals were of reagent grade. Hydrogen and nitrogen gases were supplied by Canadian Liquid Air Co.

As in previous investigations (10, 11) the rate of hydrogenation of $Cr_2O_7^=$ was used as a measure of the rate of catalytic activation of H_2. The equipment and experimental procedure have been described earlier (10, 11). When the solutions contained chloride, a titanium liner was placed in the autoclave and the stainless steel stirrer, thermocouple well, and sampling tube were replaced by titanium counterparts to avoid corrosion.

To follow the reaction, the solution was sampled periodically and analyzed for $Cr_2O_7^=$, usually by measuring the optical density at 3500 Å with a Beckman DU spectrophotometer. This procedure was not suitable for chloride-containing solutions because of interference from cupric chloride complexes which absorb light of this wave length. $Cr_2O_7^=$ was determined in such solutions by a volumetric method based on adding an excess of $FeSO_4$ and back-titrating with $KMnO_4$. The cupric content of the solutions was determined electrolytically.

In each experiment, prior to introduction of the H_2, the solution was allowed to remain in the autoclave under N_2 for a period of time comparable with the duration of the subsequent reaction. The rate at which $Cr_2O_7^=$ was consumed under these conditions, by side reactions with the complexing reagent or with the metal reaction vessel, was determined and subtracted from the subse-

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[2]*Holder of a National Research Council Studentship, 1954–55.*

quently measured rate of consumption in the presence of H_2 to obtain the rate of reaction with H_2. This correction was usually small, in most cases less than five per cent of the latter rate. Exceptions to this rule were encountered with solutions containing formate and glycine, whose rates of reaction with $Cr_2O_7^=$ under certain conditions were of the same order as that of H_2. The estimation of the latter rate in these systems was therefore subject to appreciable error.

RESULTS AND DISCUSSION

In all the experiments for which results are reported, the rate of disappearance of $Cr_2O_7^=$ was found to be of zero order in the concentration of the latter. Typical rate plots, obtained for various solutions, are shown in Fig. 1 and are

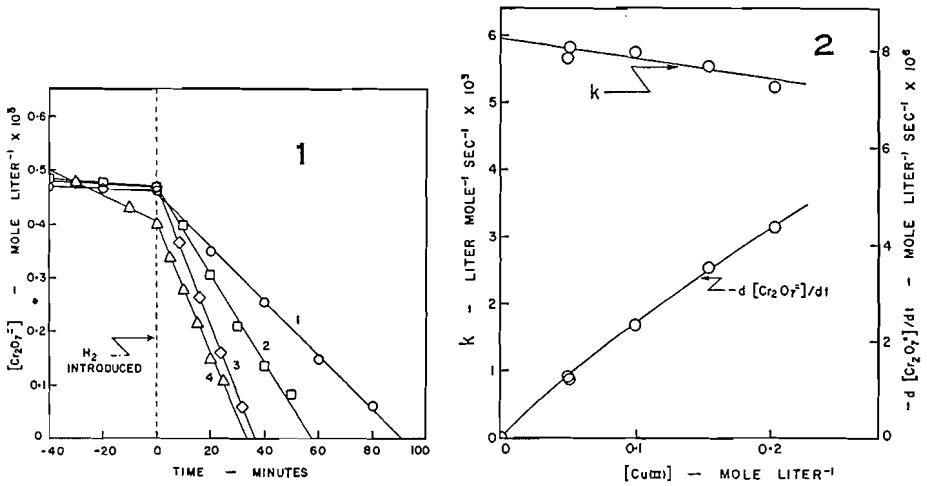

FIG. 1. Typical rate plots for reaction of H_2 with $Cr_2O_7^=$ in presence of various cupric complexes. H_2 partial pressure, 20 atm. 1. Ethylenediamine (0.05 *M* Cu^{++}, 0.20 *M* EDA, pH 4.0, 130° C.). 2. Chloride (0.10 *M* Cu^{++}, 1.0 *M* Cl^-, 110° C.). 3. Sulphate (0.10 *M* Cu^{++}, 0.10 *M* $SO_4^=$, 110° C.). 4. Glycine (0.05 *M* Cu^{++}, 0.05 *M* Gl, pH 3.5, 130° C.).
FIG. 2. Dependence of rate on cupric propionate concentration. 100° C. 20 atm. H_2.

of the same form as those reported earlier for cupric perchlorate (11) and cupric acetate (10).

The reaction between $Cr_2O_7^=$ and H_2 is represented by:

$$Cr_2O_7^= + 3H_2 + 8H^+ \rightarrow 2Cr^{+++} + 7H_2O. \qquad [1]$$

Using this stoichiometric relation, the rate of consumption of H_2 ($-d[H_2]/dt$) was determined from the measured rate of disappearance of $Cr_2O_7^=$ and expressed in terms of an apparent rate constant, k, defined by:

$$-d[H_2]/dt = -3d[Cr_2O_7^=]/dt = k[\text{Cu (II)}]\,[H_2] \qquad [2]$$

where [Cu (II)] is the total cupric ion concentration (including simple and complex forms) in the solution.

A kinetic relation of this form was shown earlier (10, 11) to apply to solutions of cupric perchlorate and cupric acetate. With solutions containing more than one cupric species, k, determined in this manner, obviously represents a weighted average of the rate constants for all the species.

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The solution concentration of hydrogen, $[H_2]$, was estimated from the measured partial pressure using available data for the solubility of H_2 in water (12, 14).

Cupric Carboxylate Complexes

Measurements of the rate of reduction of $Cr_2O_7^=$ by H_2 in the presence of various cupric carboxylate salts are reported in Table I.

TABLE I

RATE OF REACTION OF H_2 WITH $Cr_2O_7^=$ IN SOLUTIONS OF VARIOUS CUPRIC CARBOXYLATE SALTS
H_2 partial pressure—20 atm.

Temp., ° C.	Solution composition, mole liter^{-1}						Reaction rate: $-d[Cr_2O_7^=]/dt$, mole liter^{-1} sec.$^{-1}$	Reaction rate: k, liter mole^{-1} sec.$^{-1}$
100.0	0.05	$CuPr_2$;	0.0	NaPr;	0.5	HPr	1.46×10^{-6}	5.75×10^{-3}
100.0	0.05	$CuPr_2$;	0.25	NaPr;	0.5	HPr	1.46×10^{-6}	5.83×10^{-3}
100.0	0.05	$CuPr_2$;	0.5	NaPr;	0.5	HPr	1.61×10^{-6}	6.33×10^{-3}
100.0	0.05	$CuPr_2$;	1.0	NaPr;	0.5	HPr	1.50×10^{-6}	5.94×10^{-3}
100.0	0.05	$CuPr_2$;	0.25	NaPr;	0.2	HPr	1.48×10^{-6}	5.90×10^{-3}
100.0	0.05	$CuPr_2$;	0.25	NaPr;	2.0	HPr	1.83×10^{-6}	7.13×10^{-3}
80.5	0.05	$CuPr_2$;	0.25	NaPr;	0.5	HPr	2.31×10^{-7}	9.16×10^{-4}
90.2	0.05	$CuPr_2$;	0.25	NaPr;	0.5	HPr	5.95×10^{-7}	2.34×10^{-3}
110.0	0.05	$CuPr_2$;	0.25	NaPr;	0.5	HPr	3.50×10^{-6}	1.37×10^{-2}
120.6	0.05	$CuPr_2$;	0.25	NaPr;	0.5	HPr	8.60×10^{-6}	3.32×10^{-2}
100.0	0.026	$CuBu_2$	0.25	NaBu	0.5	HBu	7.70×10^{-7}	5.82×10^{-3}
100.0	0.052	$CuBu_2$	0.25	NaBu	0.5	HBu	1.53×10^{-6}	5.86×10^{-3}
100.0	0.10	$CuFo_2$	0.25	NaFo	0.25	HFo	9.8×10^{-7}	1.8×10^{-3}
100.0	0.10	$CuFo_2$	0.25	NaFo	0.25	HFo	9.6×10^{-7}	1.8×10^{-3}
100.0	0.01	CuSu	0.25	Na_2Su	0.25	H_2Su	1.3×10^{-7}	2.8×10^{-3}
100.0	0.01	CuSu	0.05	Na_2Su	0.60	H_2Su	1.1×10^{-7}	2.2×10^{-3}
100.0	0.01	CuMa	0.125	Na_2Ma	0.015	H_2Ma	5.3×10^{-8}	1.1×10^{-3}
100.0	0.002	CuFu	0.025	Na_2Fu	0.125	H_2Fu	2.7×10^{-8}	2.5×10^{-3}

The results for cupric propionate ($CuPr_2$)* parallel those obtained earlier for $CuAc_2$ suggesting that the mechanism of activation of H_2 in the two systems is essentially the same. Fig. 2 shows that the rate is nearly proportional to the $CuPr_2$ concentration, a slight tendency being apparent for the rate constant, k, to decrease at higher $CuPr_2$ concentrations. A similar effect in the $CuAc_2$ system (10) was attributed to a lowering of the solubility of H_2. The fact that the rate is essentially independent of the concentrations of NaPr and HPr, over a wide range, suggests that the catalytic activity is associated with a fully complexed cupric species. In the case of cupric acetate it has been suggested that the principal active species is the undissociated $CuAc_2$ molecule. By analogy, the active species in the present case is probably $CuPr_2$, although the possibility of participation of other complexes with catalytic activities of the same order as $CuPr_2$ is not excluded.

At 100° C., the catalytic activity of $CuPr_2$ in propionate-buffered solutions ($k \approx 6.0\times10^{-3}$ liter mole^{-1} sec.$^{-1}$) was found to be about 20% higher than that determined earlier for $CuAc_2$ ($k = 5.0\times10^{-3}$ liter mole^{-1} sec.$^{-1}$) and about

**The following abbreviations are used in this paper: Pr–propionate; Bu–butyrate; Ac–acetate; Fo–formate; Su–succinate; Ma–maleate; Fu–fumarate; Gl–glycinate; EDA–ethylenediamine.*

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150 times as great as that for the uncomplexed Cu^{++} ion ($k = 4.1\times10^{-5}$ liter mole^{-1} sec.$^{-1}$). Rate measurements for $CuPr_2$ at temperatures between 80° and 120° C. gave a good Arrhenius plot from which an apparent activation energy of 24.8±0.8 kcal./mole and a frequency factor of 2×10^{12} liter mole^{-1} sec.$^{-1}$ ($\Delta S^{\ddagger} = -4.7$ e.u. at 100° C.) were calculated. These values are in good agreement with those reported earlier for $CuAc_2$ (10).

Two experiments with $CuBu_2$ in butyrate-buffered solutions yielded rates identical with those for $CuPr_2$.

Measurements of the rate of activation of H_2 in formate-buffered solutions were subject to large errors because of complications arising from side reactions between formate and $Cr_2O_7^{=}$. The rate at 100° C. ($k = 1.8\times10^{-3}$ liter mole^{-1} sec.$^{-1}$) was about one third that for $CuAc_2$ and the higher carboxylate complexes. This may reflect the fact that complexing between Fo^{-} and Cu^{++} is incomplete, consistent with the higher dissociation constant of formic acid. Similar considerations apply to cupric fumarate and cupric maleate.

The catalytic activity of succinate-buffered cupric solutions ($k \approx 2.5\times10^{-3}$ liter mole^{-1} sec.$^{-1}$ at 100° C.) was about one half that for $CuAc_2$. It is probable that the CuSu complex has a chelate structure.

Cupric Sulphate

The results for cupric sulphate are summarized in Figs. 3 and 4. It is seen that addition of Na_2SO_4 was found to increase the catalytic activity of Cu^{++}, presumably the result of complex formation.* It has been suggested that only the first stage of association, i.e.

$$Cu^{++} + SO_4^{=} \rightleftharpoons CuSO_4, \qquad [3]$$

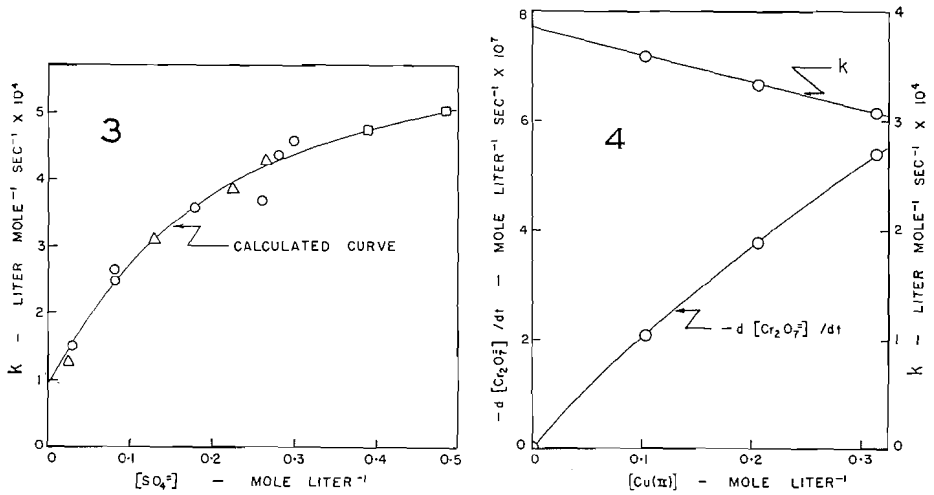

FIG. 3. Dependence of rate on $SO_4^{=}$ concentration. 0.10 *M* Cu^{++}, 20 atm. H_2. 110° C. Experimental points: ○ Total ionic strength held constant at 1.0; $[HSO_4^{-}] = 0$. □ Total ionic strength variable (>1); $[HSO_4^{-}] = 0$. △ $[HSO_4^{-}] + [SO_4^{=}] = 0.32$ *M*.

FIG. 4. Dependence of rate on cupric ion concentration in sulphate solution. 0.25 *M* $SO_4^{=}$, 0.10 *M* HSO_4^{-}, 20 atm.H_2, 110° C.

**Since sodium perchlorate was found to be without effect on the rate of catalytic activation of H_2 by cupric perchlorate, it seems reasonable to interpret the effects obtained on adding other sodium salts in terms of complexing of the anions with Cu^{++}.*

is important (7, 9), and that higher cupric sulphate complexes are not formed to an appreciable extent. The failure of the curve in Fig. 3 to level off suggests that complexing is incomplete at $SO_4^=$ concentration as high as 0.5 M./liter.

Consistent with the above interpretation, it was found that the experimental results could be fitted by a relation of the form:

$$k = (k_1[Cu^{++}] + k_2[CuSO_4])/[Cu\ (II)] \quad [4]$$

where k_1 and k_2 represent the specific rate constants for the activation of H_2 by Cu^{++} and $CuSO_4$ respectively. k_1 is known from measurements in perchlorate solution (11) and has a value of 1.0×10^{-4} liter mole^{-1} sec.$^{-1}$ at 110° C.

From equation [3], Cu^{++} and $CuSO_4$ are related by

$$[CuSO_4]/[Cu^{++}]\,[SO_4^=] = K \quad [5]$$

while

$$[Cu^{++}] + [CuSO_4] = [Cu\ (II)]. \quad [6]$$

The best correspondence between a curve for k, calculated from equations [4], [5], and [6], and the experimental points (shown in Fig. 3) was obtained using the following values: $k_2 = 6.5\times10^{-4}$ liter mole^{-1} sec.$^{-1}$ at 110° C. (i.e. about six times as great as k_1) and $K = 6.7$ liter mole^{-1}. The excellent fit lends support to these values. However, some uncertainty arises through neglect of activity coefficients and of the effect of variable salt concentration on the solubility of H_2. It is of interest that the above value of K, derived from the kinetic results at 110° C., is of the same order as the room temperature value ($\approx$4.5 liter mole^{-1} for ionic strength of unity) estimated by a spectrophotometric method (9).

Cupric Chloride Complexes

The promoting influence of Cl^- on the catalytic activity of Cu^{++} at 110° C. (Fig. 5) is attributed to the formation of cupric chloride complexes. It is probable that in the region above 1 M./liter Cl^-, where the rate levels off, the cupric ion is fully complexed, i.e. exists as $CuCl_4^=$. Hence it seems reasonable

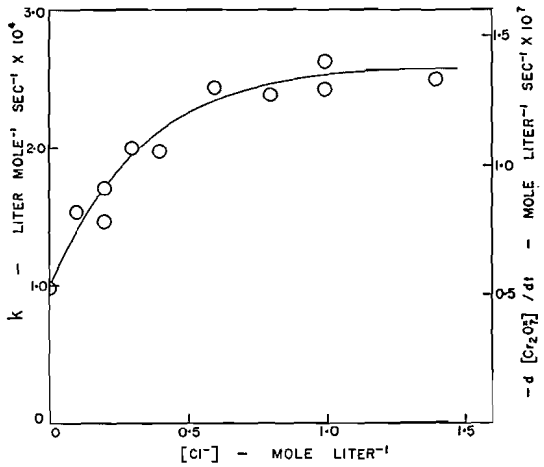

FIG. 5. Dependence of rate on Cl^- concentration. 0.10 M Cu^{++}, 20 atm. H_2, 110° C.

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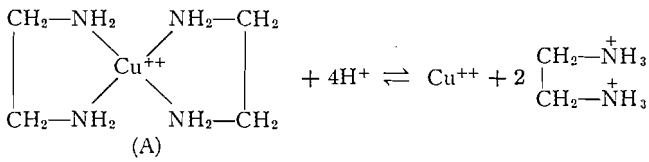
to attribute the measured value of k in this region to this complex.* This value (2.5×10^{-4} liter mole^{-1} sec.$^{-1}$) is about 2.6 times as great as for the uncomplexed Cu^{++} ion.

At constant Cl^- concentrations the rate was found to be directly proportional to the total Cu (II) concentration confirming that the catalytic activity is associated with the cupric species.

Cupric Ethylenediamine Complexes

The extent of complexing between Cu^{++} and EDA is a function of the H^+ concentration, i.e.



(A) [7]

The variation of k with pH, shown in Fig. 6, thus reflects a variation in the extent of complexing of the Cu^{++} ion.

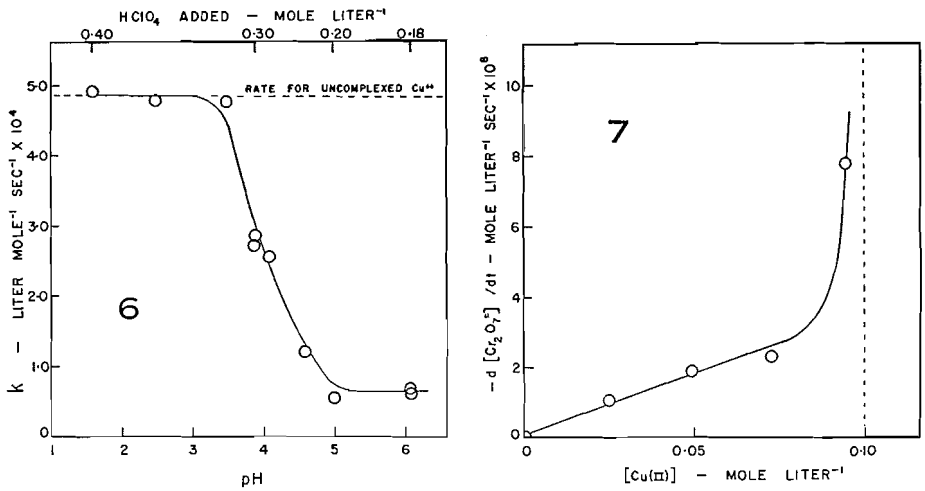


FIG. 6. Effect of pH on rate in cupric ethylenediamine solutions. 0.05 M Cu^{++}, 0.20 M EDA, 20 atm. H_2, 130° C. (pH measured at room temperature).

FIG. 7. Dependence of rate on cupric ion concentration in ethylenediamine solution. 0.20 M EDA, 20 atm. H_2, 130° C., pH 6 (measured at room temperature).

At low pH (<3, measured at room temperature) dissociation of the complex is apparently complete and the observed value of k approaches that for the uncomplexed Cu^{++} ion. Increasing the pH (by decreasing the amount of added $HClO_4$) results in a lowering of the rate, presumably reflecting the lower

**Spectrophotometrically determined values of the complexity constants of cupric chloride complexes at room temperature (8) suggest that higher Cl^- concentrations would be required to achieve complete complexing. However, it has been pointed out that these values probably increase with temperature (13).*

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catalytic activity of the $Cu(EDA)_2^{++}$ complex (A). At high pH (>5) the rate levels off at a value ($k \approx 0.6\times10^{-4}$ liter mole^{-1} sec.$^{-1}$ at 130° C.), which is about one eighth that for the uncomplexed Cu^{++} ion at the same temperature. Room temperature values of the complexity constants (6) suggest that in this region complexing is essentially complete, all the Cu (II) being present as the $Cu(EDA)_2^{++}$ complex; hence it seems reasonable to associate the measured value of the k with this complex.

This interpretation is consistent with the results shown in Fig. 7. In a series of experiments in which the Cu (II) concentration was increased while the total EDA concentration was held constant, the rate (and the apparent value of k) rose sharply as the ratio [Cu (II)]: [EDA] approached the value 0.5.

Cupric Glycinate Complexes

Figs. 8 and 9 depict the effect of Gl on the rate of catalytic activation of H_2 by Cu^{++} in solutions of different pH.

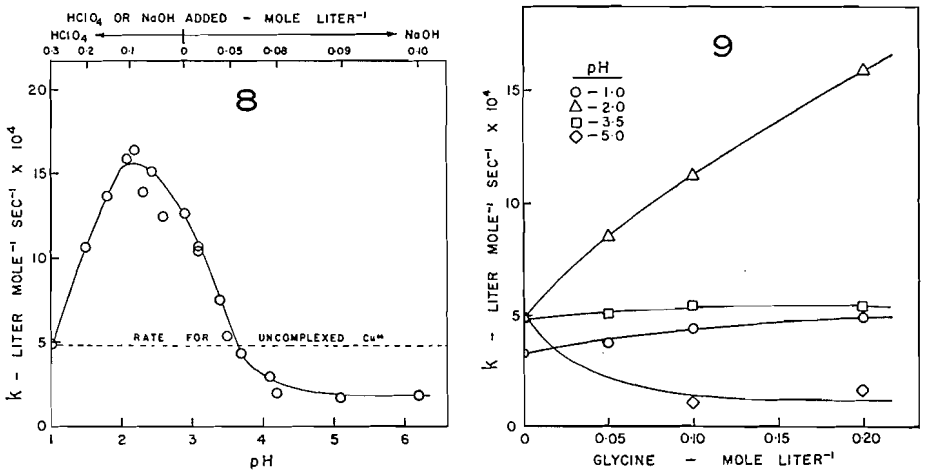
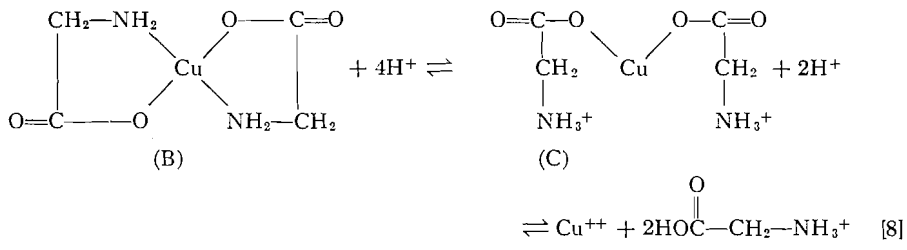


FIG. 8. Effect of pH on rate in cupric glycine solution. 0.05 *M* Cu^{++}, 0.20 *M* Gl, 20 atm. H_2, 130° C. (pH measured at room temperature).

FIG. 9. Dependence of rate on glycine concentration. 0.05 *M* Cu^{++}, 20 atm. H_2, 130° C. (pH adjusted with NaOH or $HClO_4$ and measured at room temperature).

In basic solutions complexing the Cu^{++} with Gl (involving formation of the $CuGl_2$ chelate complex) is essentially complete (6). However, with decreasing pH it is probable that the complex undergoes dissociation, passing through a number of intermediate stages including the following:



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Consistent with this it was found that at low pH (≈ 1), the value of k approaches that for the undissociated Cu^{++} ion (Fig. 8) and is essentially independent of the Gl concentration (Fig. 9).

In the region of high pH (>3.5), k decreases with increasing pH (Fig. 8) and with increasing Gl concentration (Fig. 9) approaching a value ($\approx 1.5 \times 10^{-4}$ liter $mole^{-1}$ $sec.^{-1}$ at 130° C.) about one third that of the uncomplexed Cu^{++} ion. This value, which presumably reflects the catalytic activity of the $CuGl_2$ complex (B), is subject to considerable uncertainty because of the competing side reactions between $Cr_2O_7^=$ and Gl (see Fig. 1).

In the region of intermediate pH (1–3.5) the measured value of k is greater than that for Cu^{++} and increases with the Gl concentration, presumably reflecting the presence of cupric carboxylate complexes such as (C). In common with the other cupric carboxylate complexes discussed earlier, the catalytic activity of this complex is apparently greater than that of the uncomplexed Cu^{++} ion.

CONCLUSIONS

The data obtained in this work have been used to compile Table II in which the various complexes, for which values of k have been determined, are arranged in order of decreasing catalytic activity. The listed values of the relative catalytic activities (that of the uncomplexed Cu^{++} ion being taken as unity) are only approximate since they are based on rate measurements at different temperatures (ranging from 100° to 130° C.) and of varying precision. Of particular interest is the fact that negative ions (such as Ac^-, $SO_4^=$, Cl^-) enhance the catalytic activity of Cu^{++} while chelating reagents containing amine groups reduce it.

TABLE II

RELATIVE CATALYTIC ACTIVITIES OF VARIOUS CUPRIC COMPLEXES

Complex	Catalytic activity*
$CuBu_2$	150
$CuPr_2$	150
$CuAc_2$	120
$CuSO_4$	6.5
$CuCl_4^=$	2.5
Cu^{++}	1
$CuGl_2$	<0.5
$Cu(EDA)_2^{++}$	0.1

**Relative to that of Cu^{++}.*

The similarity of the pattern of kinetic behavior for the different cupric complexes suggests that they all activate H_2 by a common mechanism. As proposed earlier (10, 11), the reduction of $Cr_2O_7^=$ may be depicted in each case as occurring through the following sequence of steps:

$$Cu\ (II) + H_2 \xrightarrow[\text{slow}]{k} X \qquad [9]$$

$$X + Cr_2O_7^= \xrightarrow[\text{fast}]{} Cu\ (II) + \text{products}. \qquad [10]$$

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The detailed configuration of the active reducing intermediate (X) has not been definitely resolved, but it has been suggested (5) that the activation process may involve electron displacement from the H_2 molecule to the catalytic Cu (II) species. Support for this suggestion is provided by the fact that the effects of the various complexing agents on the catalytic activity, noted above, follow the same general pattern as has been observed for other reactions between metal ions (such as isotopic electron exchange) which are believed to occur by electron transfer mechanisms. Such reactions are commonly catalyzed by complexing anions (1, 3, 15).

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UNIT CELL, SPACE GROUP, AND INDEXED X-RAY DIFFRACTION POWDER DATA FOR POTASSIUM HYDROGEN MALONATE, $KHC_3H_2O_4$[1]

By M. P. Gupta[2] and W. H. Barnes

The crystal structure of malonic acid has been the subject of two investigations (1, 2) but the configuration of the malonate group has not been determined in detail. In the hope that the introduction of a heavy atom may assist in the establishment of phase angles, a study of potassium hydrogen malonate has now been undertaken. Considerable delay, however, is anticipated before the work on the structure can be completed. The unit cell constants, space group, and X-ray diffraction powder data, therefore, are given in the present note as an aid to the identification of the acid salt, and the opportunity is taken of recording an interesting observation regarding the preparation of dipotassium malonate.

According to Groth (3), crystals of potassium hydrogen malonate, $KHC_3H_2O_4$, are monoclinic prismatic with $a:b:c = 1.1981:1:0.8121$, $\beta = 136°52'$, and show the forms {110}, {001}, {011}, {010}. In this laboratory the acid salt has been prepared by mixing aqueous solutions containing the appropriate stoichiometric proportions of malonic acid and potassium hydroxide, respectively, and allowing crystallization to proceed by evaporation of the solvent at room temperature. The crystals thus obtained have predominant forms corresponding to those designated {001} and {110} by Groth.

Zero-level precession photographs, taken with Mo K_α radiation ($\lambda = 0.7107$Å), along all three principal axes show that the diffraction symmetry is $2/mC-/-$. The unit cell constants are $a = 13.75$, $b = 11.61$, $c = 4.79$ Å, $\beta = 136°12'$. The axial ratio, $a:b:c = 1.184:1:0.4125$, is in reasonable agreement with that given by Groth if the latter's c/b ratio is divided by two. The density, measured at ~22°C. by flotation in mixtures of methylene iodide and toluene, is 1.81 gm./ml. There are, therefore, four molecules of $KHC_3H_2O_4$ in the unit cell; calculated density, 1.79 gm./ml.

Three space groups are compatible with the observed diffraction symmetry. Of these, $C2/m$, with eight general positions, may be eliminated from further consideration on the grounds that there are only four molecules of $KOOC.CH_2.COOH$ in the unit cell and each of these obviously must be asymmetric. Although no response was obtained from the crystals in a piezoelectric test, definite significance cannot be attached to this observation. An attempt was made to distinguish between the two other possible space groups $C2$ and Cm, on the basis of the statistical distribution of reflection intensities (4) in the $\{h0l\}$ zone. In the plot of $N(z)\%$ against $z\%$(2) the points at $z\% = 20$, 30, 40, 50, 90, 100 lie very close to the acentric curve, that at $z\% = 10$ is midway

[1]*Issued as N.R.C. No. 3870.*
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between the acentric and centric curves, while those at $z\% = 60, 70, 80$ agree better with the centric curve. These results are not completely free of ambiguity but they do strongly suggest an acentric distribution in the $\{h0l\}$ zone, and hence the space group Cm for the crystal structure. Wilson's ratio (5), $\rho = \langle|F|\rangle^2/\langle I\rangle = 0.716$, unfortunately is almost exactly the mean of the theoretical values for centric (0.637) and acentric (0.785) distributions. The forms observed on the crystals are too few for definite conclusions from the crystal morphology but the crystal class appears to be m, again suggesting Cm (rather than $C2$) as the space group.

A better choice of the unit cell (with $c < a < b$ and β closer to 90°) than that corresponding with Groth's orientation is obtained by application of the transformation matrix 102/010/001. The dimensions of the new cell are $a = 9.52$, $b = 11.61$, $c = 4.79$ Å, with $\beta = 92°6'$. There are four molecules in this unit cell, and the probable space group, as before, is Cm.

A powder photograph of potassium hydrogen malonate is reproduced in Fig. 1. It was obtained with Co K_α radiation ($\lambda = 1.790$Å) in a cylindrical

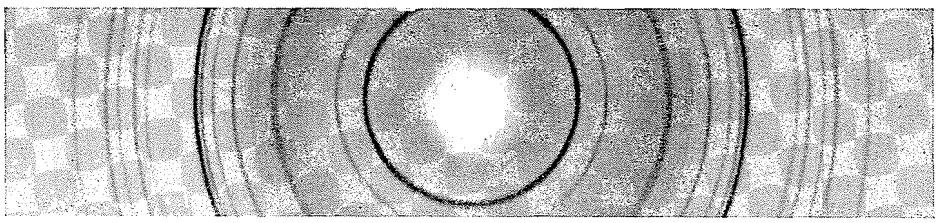

FIG. 1. X-ray diffraction powder photograph of potassium hydrogen malonate, $KHC_3H_2O_4$. (Camera diameter: 114.6 mm.; radiation: Co K_α, $\lambda = 1.790$Å.)

camera (114.6 cm. diameter), Straumanis film mounting, apparatus "cut-off" 20Å. Only the transmission section of the film is shown although the pattern extends almost to the limit of the back-reflection region. The measured spacings (d) and the visually-estimated relative intensities (I/I_1) of the lines of the powder pattern are recorded in Table I, where B identifies lines that were broader than the average, and an asterisk (in the column d(Obs.)) indicates the possible presence of a line the intensity of which was too low ($I/I_1 < 1$) for accurate determination of d. The lines of the pattern have been indexed for $d > 2.00$Å on the basis of the unit cell constants given in the preceding paragraph.

In case it should be observed in other laboratories, a very weak line of $d = 4.56$Å, which cannot be indexed, appeared in the powder photographs of two samples from the same preparation of potassium hydrogen malonate. Because this line is of significantly different relative intensity in the two films it was presumed to be due to the presence of an impurity; this was confirmed by its absence from a powder photograph of comparable density obtained from a second specimen of the salt. The spurious line cannot be due to potassium hydroxide, potassium carbonate, or malonic acid because the

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powder patterns of none of these compounds have a strong line in the appropriate 2θ region. It was considered, therefore, that it might perhaps indicate the presence of a trace of the neutral salt.

TABLE I

X-RAY DIFFRACTION POWDER DATA (INDEXED FOR $d > 2$Å)

I/I_1	d(Å) Obs.	d(Å) Calc.	hkl	I/I_1	d(Å) Obs.	d(Å) Calc.	hkl	I/I_1	d(Å) Obs.	d(Å) Calc.	hkl
100	7.32	7.36	110	1	2.23	2.22	$24\bar{1}$	2	1.59		
30	5.78	5.81	020	—	—	2.21	$022, 33\bar{1}$	3	1.49		
	*	4.79	001	40	2.19	2.20	420	8	1.47		
—	—	4.76	200	1	2.18	2.18	241	10	1.44		
30	4.02	4.07	$11\bar{1}$			2.17	$20\bar{2}$	2	1.41		
40	3.92	3.96	111	1	2.15	2.16	$331, 40\bar{1}$	3B	1.39		
20	3.66	3.69	021	5	2.10	2.11	202	10	1.34		
		3.68	220			2.10	401	3	1.30		
20	3.56	3.58	130	—	—	2.05	$15\bar{1}$	1	1.26		
1	3.47	3.44	$20\bar{1}$	30	2.03	2.03	$151, 22\bar{2}$	1	1.25		
45	3.30	3.31	201				$42\bar{1}$	8B	1.23		
30	3.05	3.06	310	1	2.01	2.00	$13\bar{2}$	3	1.22		
1	2.98	2.96	$22\bar{1}$	8	1.97			1	1.21		
40	2.92	2.90	040	8	1.92			10	1.20		
75	2.88	2.89	$13\bar{1}$	2	1.90			3B	1.19		
		2.88	221	2	1.87			3	1.17		
3	2.83	2.85	131	8	1.85			3	1.16		
5	2.59	2.62	$31\bar{1}$	3	1.83			2	1.13		
1	2.52	2.54	311	1	1.78			2	1.12		
2	2.47	2.48	041, 240	10	1.76			2	1.10		
25	2.45	2.45	330	15B	1.72			2	1.09		
35	2.37	2.39	002	15	1.70			1	1.08		
		2.38	400	5	1.68			2	1.06		
1	2.31	2.30	$11\bar{2}$	10	1.65			2	1.05		
25	2.26	2.26	112, 150	15	1.63			5	1.02	($K_{\alpha 1}$)	

Two attempts were made to prepare dipotassium malonate by mixing solutions containing the base and the acid in the proportions of two moles of potassium hydroxide to one mole of malonic acid. In each case the resulting solution was boiled and set aside at room temperature. Both preparations yielded poorly-formed crystals from an oily, viscous liquid which had the usual appearance of a concentrated solution of potassium hydroxide. Both batches of crystals gave powder photographs identical with that obtained from potassium hydrogen malonate. Solutions of potassium hydroxide and malonic acid containing the base and the acid in the molar proportions of 3: 1 (i.e., 50% excess KOH) then were mixed and the solvent was evaporated by boiling until crystallization commenced. When cooled to room temperature the mixture had the same appearance as the previous preparations, but, upon stirring vigorously, almost instantaneous conversion to a solid mass occurred. The solid was brought back into solution by the addition of distilled water, and the volume was reduced by boiling until it was estimated that crystallization would not take place until the temperature was reduced almost to that of the room. No solid phase appeared, however, on cooling to about 22°C., but

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crystallization was initiated by storage for a short time at 5°C. These crystals grew very rapidly at 22°C. into short, thick prisms of about 3 mm. cross-section, and the supernatant liquid was water-like in appearance. The crystals were reduced to powder and taken up in a capillary tube in a dry box because they proved to be somewhat deliquescent. The powder pattern of this material is not the same as that of the acid salt, nor does it have a strong line corresponding to $d = 4.56$Å.

The powder photograph of this new solid phase is not reproduced in the present note because, although it presumably represents that of dipotassium malonate, the composition of the crystals and the degree of possible hydration have not been determined. The large excess of KOH required for the formation of the neutral salt, and the tendency of the solution to supersaturation, suggest that a study of the reaction between potassium hydroxide and malonic acid, and a crystal structure determination of dipotassium malonate, might be of considerable interest. In order not to delay the investigation of the structure of potassium hydrogen malonate, however, the examination of the neutral salt has been discontinued for the present, and it has not been considered worth while to make further attempts to identify the impurity giving rise to the extraneous line of $d = 4.56$Å in the powder patterns of one of the two preparations of the acid salt.

Mr. B. J. Cowick assisted with the powder investigations.

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APPLICATION OF THE WISHAW–STOKES EQUATION TO THE CONDUCTANCES OF POTASSIUM CHLORIDE SOLUTIONS AT 25° C.

By A. N. Campbell and L. Ross

We have determined the conductances, densities, and viscosities of 2, 3, and 4 normal potassium chloride solutions; the latter concentration is almost the highest that can be attained at 25°. Campbell and Kartzmark (2) had previously calculated the conductances of potassium chloride solutions, using the equation of Wishaw and Stokes (5):

$$\Lambda = \left(\Lambda^\circ - \frac{B_2\sqrt{C}}{1+B\mathring{a}\sqrt{C}}\right)\left(1 - \frac{B_1\sqrt{C}.F}{1+B\mathring{a}\sqrt{C}}\right)\frac{\eta^\circ}{\eta}.$$

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The meanings of the symbols in the above equation are given in the original paper. Campbell and Kartzmark obtained very good agreement between the observed and calculated conductances, up to a concentration of 1 normal, using the experimental values of the International Critical Tables, and an å value (distance of closest approach) of 4.6 Å.

In the present note, we have recalculated the results, using for Λ° the very accurate figure of Gunning and Gordon (3) (Λ° = 149.88 mhos) and using two different values of å, viz. 3.3 Å and 4.6 Å. The value 3.3 Å is recommended by Stokes himself (4) for dilute solutions, but we consider that the value 4.6 Å is just as good in the dilute region and reproduces the results for concentrated solutions much better than the lower value. In our recalculation, for dilute solutions, we have used the results of Gunning and Gordon (3) wherever they were applicable. Our technique has often been described. The complete results, both our own and the literature values, are contained in the table.

TABLE I

OBSERVED AND CALCULATED EQUIVALENT CONDUCTANCES OF KCl SOLUTIONS
t = 25.0° C.

C, moles per liter	Density, gm. per ml.	Relative viscosity (H_2O = 1.000)	Λ_{exp}, mhos	Λ_{calc}		α	
				å = 3.3	å = 4.6	å = 3.3	å = 4.6
0.0000	Viscosity and density as in literature		149.88	149.91	149.86	0.999	1.000
0.0005			147.79	147.82	147.78	0.999	1.000
0.0010			146.95	146.99	146.91	0.999	1.000
0.0020			145.79	145.86	145.90	0.999	0.999
0.0050			143.59	143.70	143.71	0.999	0.999
0.0100			141.30	141.41	141.68	0.999	0.997
0.0200			138.34	138.39	138.91	0.999	0.996
0.0500			133.37	133.09	134.19	1.002	0.994
0.1000			128.96	127.98	129.88	1.008	0.993
0.2000			123.90	121.95	125.00	1.016	0.991
0.5000			117.20	112.83	117.29	1.039	0.999
1.0000			111.90	105.30	111.96	1.063	0.999
2.0050	1.087	1.005	105.81	96.95	104.53	1.091	1.012
3.0000	1.130	1.030	100.38	89.99	98.04	1.115	1.024
3.9590	1.169	1.069	94.59	83.55	91.77	1.132	1.031

The table is almost self-explanatory. The values of $\alpha = \Lambda_{obs}/\Lambda_{calc}$ have no theoretical significance; they merely represent the discrepancy between observed and calculated results. The figures for observed and calculated conductances are plotted in the diagram (Fig. 1).

It is difficult to see why so "normal" a substance as potassium chloride fails to agree with the Wishaw–Stokes equation, as contrasted with the remarkable agreement for lithium nitrate (1). For potassium chloride the discrepancy amounts to 3% at 3.96 N (using å = 4.6 Å) and this is certainly much better than is given by any other conductance equation but we had hoped for something better. It may be that the weakness lies in using the bulk viscosity instead of some related function, the bulk viscosity being somewhat too great a dividing factor. We still think, however, that the Wishaw–Stokes extension of the Debye–Hückel equation is by far the most significant contribution to

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the theory of electrolytic conductance that has been made since the inception of the Debye–Hückel theory.

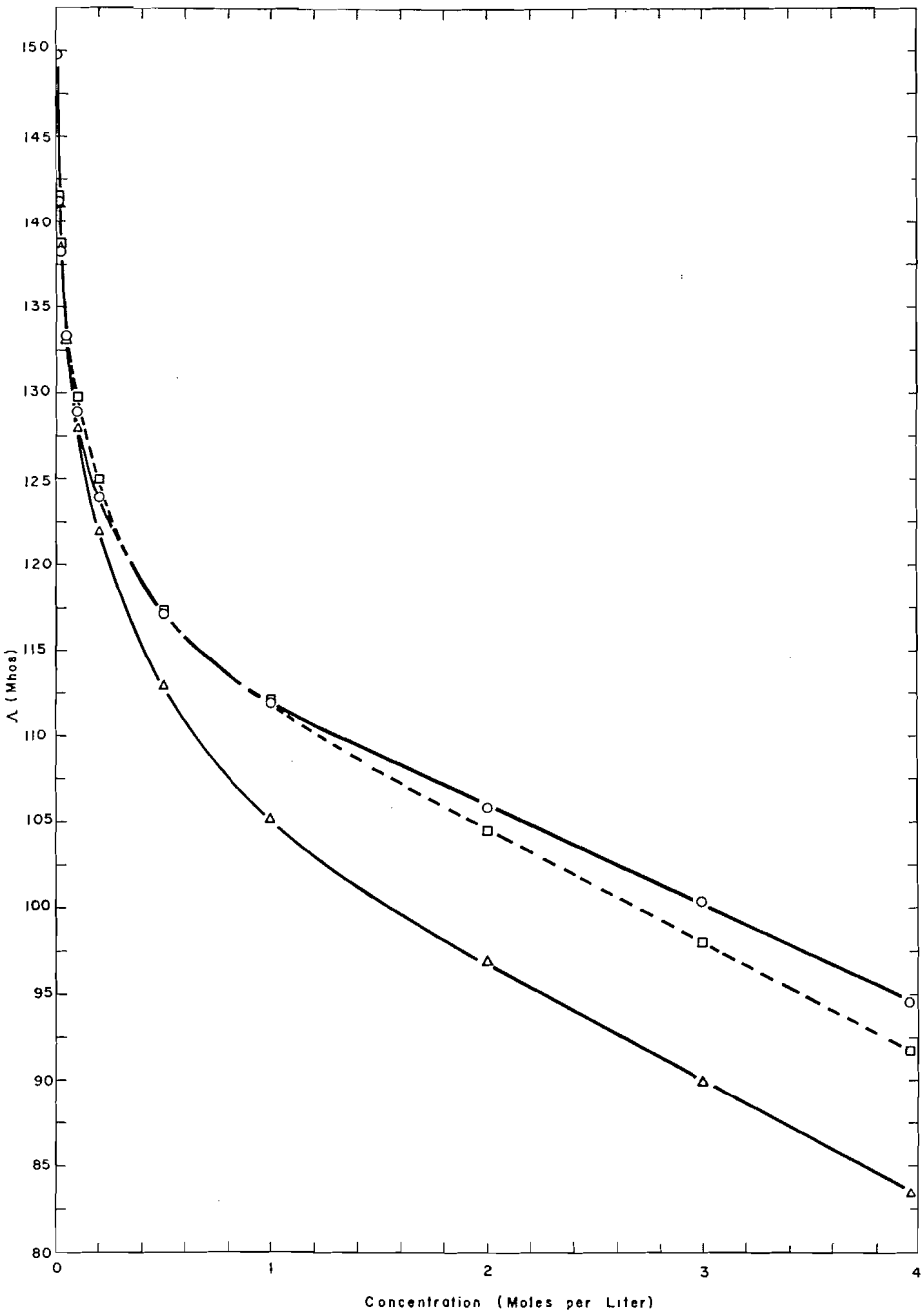

FIG. 1. Equivalent conductance versus concentration.
○ Experimental values for Λ.
△ Calculated values for Λ using å = 3.3.
□ Calculated values for Λ using å = 4.6.

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A NEW METHOD FOR PREPARING HYDROXYETHYL ETHERS OF GLUCOSE[1]

BY W. P. SHYLUK[2] AND T. E. TIMELL

ABSTRACT

Three monosubstituted hydroxyethyl ethers of D-glucose have been synthesized by a novel method involving reduction of the corresponding carboxymethyl derivatives with lithium aluminum hydride. This technique also allowed introduction for the first time of hydroxyethyl substituents containing polyethylene oxide chains of a definite length in the glucose molecule, as exemplified by the synthesis of 3-*O*-hydroxyethoxyethyl-D-glucose.

The quantitative paper chromatographic technique has recently been applied to distribution studies on hydroxyethylcellulose (1). In order to obtain the hydroxyethyl derivatives of glucose which were needed as reference compounds, a glucose derivative with the appropriate hydroxyl groups unsubstituted was reacted with ethylene oxide in the presence of alkali. This method of preparation was, however, hampered by the fact that further reaction of the hydroxyethyl group to give polyethylene oxide substituents could not be controlled.

$$ROCH_2CH_2OH + n\overset{O}{\diagup\diagdown}CH_2{-}CH_2 \rightarrow RO(CH_2CH_2O)_nCH_2CH_2OH$$

The synthesis of some carboxymethyl derivatives of glucose has recently been described (3). It has been found that the intermediates which were used for this purpose can be converted by reduction with lithium aluminum hydride into the corresponding hydroxyethyl derivatives of glucose. By repeated carboxymethylation and reduction of the latter, polyethylene oxide substituents of definite length can also be introduced.

$$ROCH_2\overset{O}{\overset{\|}{C}}OCH_3 \xrightarrow{LiAlH_4} ROCH_2CH_2OH \xrightarrow[2.\ BrCH_2\overset{O}{\overset{\|}{C}}OCH_3]{1.\quad Na} ROCH_2CH_2OCH_2\overset{O}{\overset{\|}{C}}OCH_3$$

$$\xrightarrow{LiAlH_4} ROCH_2CH_2OCH_2CH_2OH \quad \text{etc.}$$

Thus, reduction of 3-*O*-carboxymethyl-1,2;5,6-di-*O*-isopropylidene-D-glucofuranose methyl ester (3) with lithium aluminum hydride in ethyl ether gave the corresponding hydroxyethyl derivative as a sirup. The latter was hydro-

[1]*Manuscript received December 27, 1955.*
Contribution from McGill University and Pulp and Paper Research Institute of Canada, Montreal, Quebec.
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lyzed to give 3-*O*-hydroxyethyl-D-glucose which gave only one spot on a paper chromatogram, corresponding to that for Creamer's (2) 3-*O*-hydroxyethyl-D-glucose. The seeds required for crystallizing the sirupy product were obtained by purification on a paper chromatogram.

Reaction of 3-*O*-hydroxyethyl-1,2;5,6-di-*O*-isopropylidene-D-glucose with sodium and methyl bromoacetate in the manner described before (3), followed by reduction, yielded 3-*O*-hydroxyethoxyethyl-1,2;5,6-di-*O*-isopropylidene-D-glucofuranose as a sirup. This compound was hydrolyzed to give a sirupy 3-*O*-hydroxyethoxyethyl-D-glucose which moved slightly faster on a paper chromatogram than a trace of unreacted 3-*O*-hydroxyethyl-D-glucose, no complete separation being effected, however.

A sirupy sample of methyl 3,5,6-tri-*O*-benzyl-2-*O*-carboxymethyl-α,β-D-glucofuranoside methyl ester (3) was reduced in the same manner. The corresponding hydroxyethyl derivative thus obtained was hydrogenated for removal of the benzyl groups and subsequently hydrolyzed to give 2-*O*-hydroxyethyl-D-glucose as a sirup, which, after fermentation, showed only one spot on a paper chromatogram.

Reduction of 6-*O*-carboxymethyl-1,2;3,5-di-*O*-methylene-D-glucofuranose methyl ester and subsequent hydrolysis yielded 6-*O*-hydroxyethyl-D-glucose as a sirup which gave only one spot on a paper chromatogram. This material was crystallized by means of seeds which were obtained after purification by paper chromatography. Brownell (1) had prepared this derivative by a different method, but was unable to crystallize the product.

As is shown in Fig. 1, the three *O*-hydroxyethyl-D-glucoses could be completely separated by paper chromatography, the best solvent system being a mixture of ethyl acetate, acetic acid, and water in the (v/v) ratio of 9:2:2.

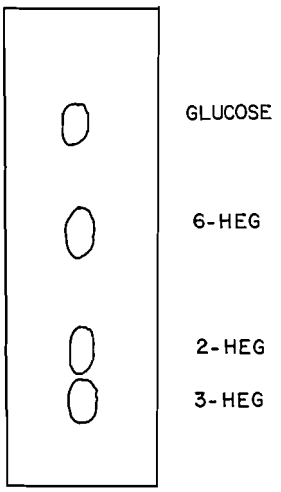

FIG. 1. Paper chromatogram of D-glucose and three *O*-hydroxyethyl-D-glucoses (HEG).

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EXPERIMENTAL

Chromatograms were run by the descending method using (1) *n*-butanol saturated with water; (2) ethyl acetate, pyridine, and water, 5:2:5; and (3) ethyl acetate, acetic acid, and water, 9:2:2. Aniline phosphate was used as the spraying reagent. Melting points were determined as referred to earlier (3).

*3-O-Hydroxyethyl-*D*-glucose*

To a solution of 3 gm. of 3-*O*-carboxymethyl-1,2;5,6-di-*O*-isopropylidene-D-glucofuranose methyl ester (3) in 50 ml. of absolute ethyl ether, an ether solution of lithium aluminum hydride was added dropwise with stirring in an atmosphere of nitrogen. After three hours at room temperature, anhydrous ethyl acetate was slowly added to decompose the excess of the hydride. Wet ethyl ether was slowly added until a coarse crystalline mass separated, after which approximately 0.5 ml. of water was added. The mixture was dried with sodium sulphate and filtered. Evaporation of the ether solution gave 2.1 gm. of a sirup, which was hydrolyzed with 2% sulphuric acid and deionized with Amberlite IR-120 and IR-4B exchange resins. Evaporation of the neutral solution *in vacuo* yielded a sirup which was found by paper chromatography (solvents No. 1 and 2) to give as the only spot one which corresponded to Creamer's sample of 3-*O*-hydroxyethyl-D-glucose.

Approximately 70 mgm. of the above sirup was applied to a sheet of 3MM paper in spots of 0.005 ml. each, after which the sheet was irrigated with solvent No. 1 for two days. Guide strips were cut from the ends, sprayed, and then used for locating the band on the remainder of the sheet, which was cut out and eluted with water. The aqueous solution was concentrated *in vacuo* to a white residue which was extracted with 2 ml. of absolute ethanol. The latter solution was evaporated to dryness, giving a sirup which crystallized when rubbed with ethanol. Further crystallization with the aid of these crystals as seeds gave 0.78 gm. of crystalline material, m.p. 122–124° C., corresponding to a yield of 50% based on the weight of the sirup hydrolyzed. Recrystallization from ethanol gave 0.40 gm. of a product, m.p. 125–126° C., $[\alpha]_D$ after 3 min., 82.8°, and at equilibrium, 51.8° (*c*, 1.4 in water). Brownell (1) reported an extrapolated initial value of 93° and an equilibrium value of 51.4° for $[\alpha]_D$.

*3-O-Hydroxyethoxyethyl-*D*-glucose*

A dry sirup of 3-*O*-hydroxyethyl-1,2;5,6-di-*O*-isopropylidene-D-glucofuranose, 1.4 gm., prepared as described above, was dissolved in 50 ml. of absolute ethyl ether and stirred with 2 ml. of dispersed sodium for 15 hr. at room temperature in an atmosphere of nitrogen. Methyl bromoacetate, 4 ml., was added, the color turning green with evolution of heat, after which the mixture was stirred for six hours at room temperature. Water, 50 ml., and ethyl ether, 50 ml., were added. The ether layer was washed twice with 25-ml. portions of water, dried over sodium sulphate, and evaporated *in vacuo* to a sirup weighing 2 gm., which was subsequently reduced with lithium aluminum hydride in absolute ethyl ether as described above. The sirupy product was hydrolyzed with 4 gm. of Amberlite IR-120 exchange resin and 8 ml. of water at reflux temperature for 12 hr. The aqueous filtrate obtained after removal of the resin

was concentrated to 1.5 ml. Paper chromatography (solvent No. 3) indicated a strong spot which was not completely separated from a weaker, slower moving spot, corresponding to that of 3-*O*-hydroxyethyl-D-glucose. When the latter compound was applied together with the reaction product, the slower moving spot became stronger while the intensity of the faster moving one appeared unchanged.

2-O-Hydroxyethyl-D-glucose

Crude, sirupy methyl 3,5,6-tri-*O*-benzyl-2-*O*-carboxymethyl-α,β-D-glucofuranoside methyl ester (3), 1.0 gm., was dissolved in 10 ml. of absolute tetrahydrofuran and an excess of lithium aluminum hydride was added. After the mixture had been refluxed for 3.5 hr., 0.8 gm. of material was isolated as described for the 3-*O*-hydroxyethyl derivative. The sirup obtained was hydrogenated at a pressure of slightly more than 1 atm. of hydrogen in 20 ml. of tetrahydrofuran in the presence of 0.3 gm. of palladium black at room temperature. The catalyst was removed by filtration and the filtrate was concentrated *in vacuo* to a sirup which was hydrolyzed in the usual way with Amberlite IR-120 exchange resin. Paper chromatography (solvent No. 3) indicated a strong spot which was assigned to 2-*O*-hydroxyethyl-D-glucose and a medium spot for glucose, which disappeared after fermentation of the aqueous solution. No attempt was made to purify this glucose derivative.

6-O-Hydroxyethyl-D-glucose

An excess of ethyl ether solution of lithium aluminum hydride was added to a solution of 1.8 gm. of 6-*O*-carboxymethyl-1,2;3,5-di-*O*-methylene-D-glucofuranose methyl ester in 50 ml. of absolute tetrahydrofuran and the mixture was refluxed for two hours under dry nitrogen. The reaction product was isolated as described for 3-*O*-hydroxyethyl-D-glucose. The sirup obtained, 1.2 gm., was refluxed with 20 ml. of 2.5% hydrochloric acid for 12 hr. The yellow solution was deionized with Amberlite IR-120 and IR-4B exchange resins, treated with Darco G-60, and evaporated *in vacuo* at 45° C. to a sirup. Crystals were obtained by applying 90 mgm. of the latter to a sheet of Whatman No. 3MM paper and by following the chromatographic procedure described above. The remaining sirup was dissolved in 0.5 ml. of ethanol, seeded, and allowed to crystallize at room temperature, resulting in 0.47 gm. of material in 32% yield, m.p. 94–101° C. Recrystallization from ethanol gave 0.16 gm. of a product, m.p. 106–107° C., $[\alpha]_D$ after 4 min., 83.5°, at equilibrium, 48.7° (*c*, 1.5 in water). Calc. for $C_8H_{16}O_7$: C, 42.8; H, 7.14%. Found: C, 42.8; H, 7.09%.

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SYNTHESIS OF FOUR CARBOXYMETHYL ETHERS OF GLUCOSE[1]

By W. P. Shyluk[2] and T. E. Timell

ABSTRACT

The 2-, 3-, and 6-*O*-carboxymethyl-D-glucoses and the 2,3-di-*O*-carboxymethyl-D-glucose have been synthesized. A solvent system was found which gave complete paper chromatographic separation of these derivatives as well as of those obtained upon hydrolysis of a carboxymethylcellulose.

The physical and chemical properties of partially substituted cellulose derivatives cannot be explained only in terms of molecular weight, polymolecularity, and degree of substitution, the distribution of the substituents along the chain molecules of cellulose also having to be considered. Various approaches in such distribution studies have been used, the most direct of which involves quantitative paper chromatography. Brownell (3) appears to have come the closest to a successful application of such a method in his work on hydroxyethylcellulose. However, in this study, as well as in similar work on methylcellulose (1, 8, 11), most of the isomeric mono- and di-substituted derivatives of glucose could not be separated.

Previous investigations on carboxymethylcellulose (6, 12, 15, 16) have indicated the desirability of a more direct approach and this study was undertaken to develop the quantitative paper chromatographic technique for this purpose. Three stages had to be considered in this connection, namely hydrolysis of the carboxymethylcellulose, separation and identification of the various carboxymethylated glucoses in the hydrolyzate, and the quantitative determination of these glucose derivatives.

The hydrolysis of carboxymethylcellulose and the stability of the carboxymethyl group to the conditions of acid hydrolysis have been previously investigated (15). For separation and identification of the seven possible carboxymethyl derivatives of glucose which conceivably could be formed by hydrolysis of a partially substituted carboxymethylcellulose, it was necessary to have these seven compounds available. The present study deals with the synthesis and separation of the 2-, 3-, and 6-*O*-carboxymethyl-D-glucoses and the 2,3-di-*O*-carboxymethyl-D-glucose.

RESULTS AND DISCUSSION

The general procedure used for introducing the carboxymethyl groups in the desired positions was to allow methyl bromoacetate to react with the sodio compound, prepared by the reaction of metallic sodium with a glucose derivative having the appropriate hydroxyl groups unsubstituted. For the preparation of the sodio derivative, advantage was taken of the greater chemical reactivity of sodium dispersions (2). Such dispersions consist of a stable sus-

[1]*Manuscript received December 27, 1955.*
Contribution from McGill University and Pulp and Paper Research Institute of Canada, Montreal, Quebec.
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pension of microscopic particles of sodium in an inert medium which has almost the same fluidity as the latter, the handling of metallic sodium thus being greatly simplified as a burette or pipette can be used. A microcrystalline semi-dispersion of sodium hydride in oil was also used for the same purpose. This reagent was very similar in its handling and chemical reactivity to the sodium dispersions, having the added advantage of being available commercially.

The following sequence of reactions was used to prepare 3-*O*-carboxymethyl-D-glucose. Reaction of 1,2;5,6-di-*O*-isopropylidene-D-glucofuranose with dispersed sodium in ethyl ether gave the corresponding sodio derivative. The latter was not isolated and an excess of methyl bromoacetate was added to the reaction mixture. Crystalline 3-*O*-carboxymethyl-1,2;5,6-di-*O*-isopropylidene-D-glucofuranose methyl ester was isolated in 61% yield. The same crystalline derivative was also obtained in a somewhat improved yield by the use of sodium hydride in oil. Hydrolysis gave 3-*O*-carboxymethyl-D-glucose as a sirup which was pure as indicated by paper chromatography.

Various analyses of the sirupy 3-*O*-carboxymethyl-D-glucose indicated that it was reasonably pure and the product obtained by treatment of this derivative with methanolic hydrogen chloride also had the correct analysis. The sample could not be induced to crystallize, however, although various techniques were tried. It seemed probable that the main factor preventing its crystallization was to be found in the complex equilibrium mixture existing in its aqueous solution, involving the α- and β-modifications of the furanose and pyranose forms in equilibrium with the *aldehydo* form as well as the two δ-lactones in the 2- and 4-positions.

For the synthesis of 2-*O*-carboxymethyl-D-glucose, a series of reactions similar to that applied by Weygand and Trauth (18) for the preparation of 2-*O*-methyl-D-glucose was used. Treatment of methyl 3,5,6-tri-*O*-benzyl-α,β-D-glucofuranoside with dispersed sodium in ethyl ether resulted in the sodio derivative, which was treated with methyl bromoacetate to give sirupy methyl 3,5,6-tri-*O*-benzyl-2-*O*-carboxymethyl-α,β-D-glucofuranoside methyl ester. Sirupy 2-*O*-carboxymethyl-D-glucose was obtained after hydrogenolysis of the latter compound, followed by acid hydrolysis and purification by adsorption on Amberlite IR-4B exchange resin and thorough washing with water. The regenerated sugar acid contained only a trace of glucose but failed to crystallize. Crystalline methyl 4,6-*O*-ethylidene-β-D-glucopyranoside 3-nitrate was also prepared in the hope that it might be used for obtaining the corresponding 2-*O*-carboxymethyl methyl ester derivative in the crystalline form. The nitrate group, however, was found to be unstable to metallic sodium.

Dimethylene glucose, the structure of which has recently been shown to be 1,2;3,5-di-*O*-methylene-D-glucofuranose (13, 14), has been used for the introduction of substituents in the 6-position of glucose (3, 9). Treatment of this derivative with dispersed sodium in dioxane gave the corresponding sodio derivative which, upon reaction with methyl bromoacetate, yielded 6-*O*-carboxymethyl-1,2;3,5-di-*O*-methylene-D-glucofuranose methyl ester in the crystalline form. Hydrolysis of the latter compound produced a chromatographically pure 6-*O*-carboxymethyl-D-glucose, which could not, however, be induced to crystallize.

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In an attempt to establish whether the Purdie reaction could be applied in the synthesis of carboxymethyl derivatives of glucose, dimethylene glucose was treated twice with methyl bromoacetate and silver oxide. A paper chromatogram showed two spots of equal intensity for 6-*O*-carboxymethyl-D-glucose and glucose after hydrolysis, thus indicating the feasibility of the procedure.

For preparation of 2,3-di-*O*-carboxymethyl-D-glucose the following reactions were used. Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside was treated with dispersed sodium to give the disodio derivative which was subsequently allowed to react with methyl bromoacetate to yield methyl 4,6-*O*-benzylidene-2,3-di-*O*-carboxymethyl-α-D-glucopyranoside methyl ester as a sirup. A paper chromatogram of the hydrolyzed material exhibited weak spots for 2-*O*-carboxymethyl-D-glucose and glucose, and an additional strong spot which was assumed to represent 2,3-di-*O*-carboxymethyl-D-glucose. Better results were obtained with sodium hydride but the Purdie reaction gave only a trace of disubstituted compound.

As shown in Fig. 1, a complete separation of the *O*-carboxymethyl-D-glucoses by paper chromatography was accomplished. As far as is known, this appears

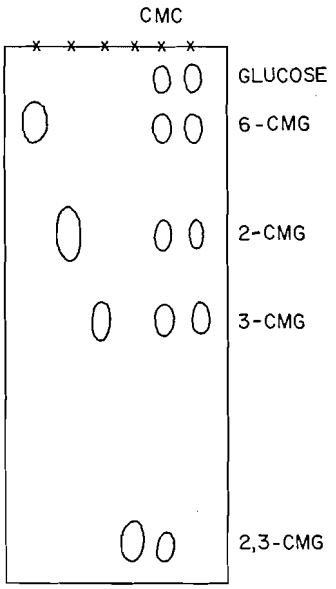

FIG. 1. Paper chromatogram of D-glucose, four *O*-carboxymethly-D-glucoses (CMG), and hydrolyzate of a carboxymethylcellulose (CMC).

to be the first instance when three isomeric monosubstituted glucose derivatives have been unambiguously separated on a paper chromatogram. The solvent system which gave this separation was composed of ethyl acetate, formic acid (87–90%), and water in the (v/v) ratio of 12: 1: 12.

The carboxymethylcellulose referred to in Fig. 1 was a specimen averaging 1.11 carboxymethyl groups per anhydroglucose unit of the chain molecules. This compound, when hydrolyzed and subjected to paper chromatography,

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gave the spots indicated, the intensity of which suggested the correctness of a previous, indirect analysis of the same sample (16). With only one disubstituted carboxymethyl glucose available nothing, of course, could be stated yet concerning the presence and nature of the disubstituted sugars present in the hydrolyzate.

EXPERIMENTAL

Although two samples of dispersed sodium were kindly supplied by U.S. Industrial Chemical Company, New York, N.Y., most of the dispersed sodium was prepared shortly before use with the aid of a Waring Blendor with a modified Pyrex jar (2). A 20% microcrystalline semidispersion of sodium hydride in Bayol 85 was obtained as a sample through the courtesy of Metal Hydrides Inc., Beverly, Mass.

For paper chromatography, the descending flow technique was applied throughout and the solvent system was the mixture mentioned above. The chromatograms were made on Whatman No. 3MM paper and aniline phosphate (4) was used to locate the spots. The thermometer employed for determining the melting points was checked against pure compounds as suggested by Bunce (5) and all values were corrected accordingly.

3-O-Carboxymethyl-1,2;5,6-di-O-isopropylidene-D-glucofuranose Methyl Ester

A. Method Using Sodium Dispersed in Toluene

An excess of dispersed sodium was added with constant stirring and in an atmosphere of nitrogen to 60 gm. of 1,2;5,6-di-*O*-isopropylidene-D-glucofuranose (17) dissolved in 575 ml. of absolute ethyl ether. After six hours at room temperature, 35.6 ml. of methyl bromoacetate was added dropwise from a burette and a vigorous exothermic reaction was observed, after which the mixture was refluxed for two hours. Water, 100 ml., was added and the resulting red aqueous layer was separated. After the ether layer had been washed with four 50-ml. portions of water, it was dried over anhydrous sodium sulphate and concentrated *in vacuo* at 50° and 75° C. to give 73.0 gm. of a crystalline product. Hydrolysis and paper chromatography showed a strong spot which was assigned to 3-*O*-carboxymethyl-D-glucose and a weak spot for glucose. Recrystallization of the crude product from isopropyl ether gave 46.7 gm. of material in 61% yield, m.p. 100–101.5° C. Four more recrystallizations from isopropyl ether removed the unreacted diacetone glucose and gave fine needles of 3-*O*-carboxymethyl-1,2;5,6-di-*O*-isopropylidene-D-glucofuranose methyl ester, m.p. 104–105° C., $[\alpha]_D$ −3.5° (*c*, 1.5 in chloroform). Calc. for $C_{15}H_{24}O_8$: C, 54.2; H, 7.28; (OCH_3), 9.34%. Found: C, 54.4; H, 7.31; (OCH_3), 9.35%.

B. Method Using Sodium Hydride in Oil

Dispersed sodium hydride, 4 ml., was added to 5 gm. of 1,2;5,6-di-*O*-isopropylidene-D-glucofuranose in 75 ml. of absolute ethyl ether. The mixture was stirred in an atmosphere of dry nitrogen at room temperature for 18 hr. Methyl bromoacetate, 5 ml., was added, causing an immediate reaction with evolution of heat. Another 5 ml. of methyl bromoacetate was added after the mixture had been stirred at room temperature for 12 hr. After additional

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stirring for 28 hr., 2 ml. of absolute methanol was added to decompose any excess of hydride, very little of which appeared to be left. Ethyl ether, 75 ml., and 50 ml. of water were added to the reaction mixture. The dark red aqueous layer formed was discarded and the ether layer was washed with four 25-ml. portions of water. The pale yellow ether solution was treated as above and yielded 8.3 gm. of a partially crystalline product (including 2.5 gm. of Bayol 85). Recrystallization from isopropyl ether gave 5.0 gm. in 78% yield of slightly colored needles, m.p. 103–104.5° C. Two more recrystallizations from the same solvent resulted in 4.2 gm. of a pure product with the same melting point and mixed melting point as the material referred to above.

*Methyl 3-O-Carboxymethyl-α-*D*-glucopyranoside Methyl Ester*

A sirup of 3-*O*-carboxymethyl-D-glucose (pure as indicated by paper chromatography), 0.93 gm., was dissolved in 75 ml. of 2.5% methanolic hydrogen chloride and 5 gm. of Drierite was added. The reaction mixture was kept at reflux temperature in a dry atmosphere for three days. The pale yellow solution was neutralized with silver carbonate and the cloudy filtrate obtained was clarified by saturating with hydrogen sulphide and heating. After filtering, the solution was concentrated *in vacuo* at 50° C. to a sirup, which was decolorized and clarified by dissolving in a small volume of methanol and treating with Darco G-60, three such treatments being necessary. The resulting sirup was dried *in vacuo* at 55° C. for two days and was found to weigh 0.82 gm. Although the product had the correct methoxyl analysis of 23.5% (theoretical 23.3%), it failed to crystallize after several months.

*3-O-Carboxymethyl-*D*-glucose*

A mixture of 7 gm. of 3-*O*-carboxymethyl-1,2;5,6-di-*O*-isopropylidene-D-glucofuranose methyl ester and 25 gm. of Amberlite IR-120 exchange resin in 25 ml. of water was stirred on a steam bath for 12 hr. The resin was filtered off and washed thoroughly with water. The combined filtrate and washings was treated with Darco G-60 and evaporated to approximately 50 ml. Freeze-drying of this solution gave 5.0 gm. of a friable resin-like material, $[\alpha]_D$ 51.2° (*c*, 1.5 in water), which was very hygroscopic. This product was chromatographically pure with regard to several solvent systems and several spraying agents. Other solutions of 3-*O*-carboxymethyl-D-glucose were evaporated to sirups which all failed to crystallize when subjected to various techniques used to induce crystallization. Calc. for $C_8H_{14}O_8$: C, 40.3; H, 5.9%. Found: C, 39.2; H, 6.0%. Titration of 64.0 mgm. in 5 ml. of water under nitrogen with 0.0222 *N* barium hydroxide and with methyl red as indicator resulted in the consumption of 12.66 ml. of barium hydroxide. This titer was equivalent to 66.9 mgm. of 3-*O*-carboxymethyl-D-glucose. Various techniques were applied to obtain sirups free of lactones, all of which, however, failed to produce the desired crystallization.

*Methyl 3,5,6-Tri-O-benzyl-2-O-carboxymethyl-α,β-*D*-glucofuranoside Methyl Ester*

Sirupy 3,5,6-tri-*O*-benzyl-α,β-D-glucofuranoside, 34 gm., was dissolved in 125 ml. of absolute ethyl ether. Dispersed sodium, 15 ml., was added dropwise

over a two-hour period with stirring and in an atmosphere of dry nitrogen, after which stirring was continued for six hours at room temperature. Methyl bromoacetate, 25 ml., was added dropwise and an exothermic reaction was observed. The mixture was stirred at room temperature for 12 hr. Water, 100 ml., and ethyl ether, 200 ml., were added to the gray reaction mixture, the color changing to red. The ether layer was washed with five 100-ml. portions of water, dried over sodium sulphate, and evaporated to 34 gm. of a light red sirup.

The product was dissolved in 100 ml. of tetrahydrofuran in a stainless steel bomb and 3 gm. of palladium black was added. Hydrogenation was effected at a pressure of 600 p.s.i. of hydrogen over a five-hour period and at 100° C. After the catalyst had been removed, 17.3 gm. of a brown sirup was obtained upon evaporation *in vacuo* of the filtrate. This material was stirred in 200 ml. of 2% sulphuric acid on a steam bath for eight hours. The hydrolyzate was extracted with eight 50-ml. portions of ethyl ether, evaporation of which yielded 4 gm. of a red, optically inactive sirup. The acid was neutralized with barium hydroxide and the barium sulphate digested on a steam bath for two hours. After centrifuging, the supernatant aqueous solution was slowly passed through a column of Amberlite IR-120 exchange resin and the latter washed with water until the effluent was neutral. Evaporation of the pale-yellow aqueous effluent *in vacuo* at 60° C. gave 9.0 gm. of a brown sirup. Paper chromatography showed a strong spot which was assigned to 2-*O*-carboxymethyl-D-glucose and a medium spot for glucose. After further purification with the aid of the same exchange resin, the final product contained only a trace of glucose.

Attempted Preparation of 2-O-Carboxymethyl-4,6-O-ethylidene-β-D-glucopyranoside 3-Nitrate Methyl Ester

Methyl 4,6-*O*-ethylidene-β-D-glucopyranoside 3-nitrate (7, 10), 1.6 gm., was stirred at room temperature under dry nitrogen with 2 ml. of dispersed sodium in 50 ml. of absolute ethyl ether for 20 hr. The orange-brown reaction mixture was cooled in an ice-bath and 10 ml. of methyl bromoacetate was added. The mixture was stirred at room temperature for one and one-half hours and at reflux for eight hours. Ethyl ether, 50 ml., was added and the ether solution was washed with three 50-ml. portions of water. The light yellow solution was dried over sodium sulphate and evaporated *in vacuo* at 40° and 90° C. to a yellow sirup weighing 0.6 gm. A spot test for organic nitrate with diphenylamine and sulphuric acid on the sirup was negative. Hydrolysis of a small amount of this material and paper chromatography indicated a strong spot for glucose and medium spots for the 2- and 3-*O*-carboxymethyl-D-glucoses and the 2,3-di-*O*-carboxymethyl-D-glucose.

6-O-Carboxymethyl-1,2;3,5-di-O-methylene-D-glucofuranose Methyl Ester

A. Method Involving Sodium Dispersed in Toluene

A solution of 1 gm. of 1,2;3,5-di-*O*-methylene-D-glucofuranose, prepared as described previously (14), in 25 ml. of absolute dioxane was treated with 2 ml. of dispersed sodium. The mixture was stirred in an atmosphere of nitrogen for

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17 hr. and was then cooled in an ice-bath, after which 0.81 ml. of absolute methanol was added. The brown, gelatinous mixture was stirred for one hour at room temperature, methyl bromoacetate, 4.5 ml., was slowly added, and the resulting reaction mixture stirred for an additional four hours. Dioxane, 50 ml., was added and the mixture was centrifuged. The dioxane solution was concentrated *in vacuo* at 50° and 90° C. to a light red sirup, which was dissolved in benzene and applied to a column of 5: 1 Magnesol–Celite. The latter was washed with 100: 1 benzene–ethanol and the slightly yellow filtrate concentrated to a sirup weighing 1.15 gm. Hydrolysis and paper chromatography of a small amount of this material indicated a strong spot which was assigned to 6-*O*-carboxymethyl-D-glucose and a weak spot for glucose. The remainder of the sirup was rubbed on a watch glass with methanol and ethyl ether, crystallization occurring after 12 hr. A solution of 1.0 gm. of the sirup in 2 ml. of methanol was cooled, seeded, and allowed to crystallize at 5° C. A crystalline material in the form of long flat rods, 0.66 gm., corresponding to a yield of 49%, was obtained. The product had a melting point of 46.5–47.5° C. and $[\alpha]_D$ 32.7° (*c*, 1.3 in chloroform) after three recrystallizations from methanol at 5° C. Calc. for $C_{11}H_{16}O_8$: C, 47.8; H, 5.84; (OCH_3), 11.2%. Found: C, 47.7; H, 5.52; (OCH_3), 11.4%.

B. Method Involving Sodium Hydride

Dispersed sodium hydride, 2 ml., was added to a solution of 1,2;3,5-di-*O*-methylene-D-glucofuranose, 1.0 gm., in 25 ml. of absolute dioxane and the mixture was stirred under nitrogen for 25 hr. at room temperature. Methyl bromoacetate, 5 ml., was added and stirring continued for another 12 hr. After addition of 50 ml. of dioxane and centrifuging, the dioxane solution was evaporated to a sirup which was rinsed once with petroleum ether. Crystallization from methanol yielded 0.35 gm. in 26% yield of crystals with a melting point of 47–48° C. Paper chromatography after hydrolysis of the crude product showed a strong spot for 6-*O*-carboxymethyl-D-glucose and a weak spot for glucose.

C. Purdie Method

A mixture of 1.0 gm. of 1,2;3,5-di-*O*-methylene-D-glucofuranose, 2 ml. of methyl bromoacetate, 1.16 gm. of silver oxide, and a small amount of Drierite was stirred at 100° C. for two hours with exclusion of moisture. Another 0.5 gm. of silver oxide was added and the reaction was continued for another hour. Chloroform was added to the cooled mixture, followed by filtration. Evaporation of the filtrate *in vacuo* gave a sirup which was treated once more with the same reagents. The product was hydrolyzed and paper chromatography indicated spots of equal intensity for 6-*O*-carboxymethyl-D-glucose and glucose.

6-O-Carboxymethyl-D-glucose

A mixture of 2.8 gm. of 6-*O*-carboxymethyl-1,2;3,5-di-*O*-methylene-D-glucofuranose methyl ester and 6 gm. of Amberlite IR-120 exchange resin in 12 ml. of water was stirred at reflux temperature for 24 hr. The resin was removed by filtration and the filtrate clarified with Darco G-60. The sirup obtained after

evaporation *in vacuo* was carefully dried over phosphorus pentoxide and failed to crystallize after one month. The material was dissolved in water for easier handling and freeze-dried to a friable, resin-like material. Paper chromatography suggested the presence of only 6-*O*-carboxymethyl-D-glucose.

Methyl 4,6-O-Benzylidene-2,3-di-O-carboxymethyl-α-D-glucopyranoside Methyl Ester

Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (7), 3.0 gm., and 5 ml. of dispersed sodium hydride were stirred in 50 ml. of anhydrous dioxane at room temperature in an atmosphere of nitrogen for 13½ hr. The thick, gray, gelatinous reaction mixture was shaken with an additional 2 ml. of sodium hydride for another 61½ hr. Methyl bromoacetate, 10 ml., was added and the mixture stirred for 46 hr. After addition of 50 ml. of chloroform and centrifuging, the supernatant solution was evaporated *in vacuo* at 60° and 75° C. to a sirup, the Bayol was poured off, and the remaining material washed with petroleum ether to yield 7.8 gm. of a sirup. Hydrolysis of a small amount of the latter and paper chromatography indicated weak spots for glucose and 2-*O*-carboxymethyl-D-glucose and an additional, strong, faster moving spot which was assigned to 2,3-di-*O*-carboxymethyl-D-glucose. The sirup failed to crystallize after several weeks during which time it was subjected to various techniques for inducing crystallization.

A similar synthesis involving sodium dispersed in toluene yielded a product which, after hydrolysis and paper chromatography, showed strong spots for glucose and 2,3-di-*O*-carboxymethyl-D-glucose and somewhat weaker spots for the 2- and 3-*O*-carboxymethyl-D-glucoses.

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THE HEATS OF CRYSTALLIZATION OF VACUUM DEHYDRATED MAGNESIUM SULPHATE HEPTAHYDRATE AND COBALTOUS CHLORIDE HEXAHYDRATE[1]

By J. W. S. Jamieson[2] and G. B. Frost

ABSTRACT

Magnesium sulphate monohydrate prepared by vacuum dehydration of the heptahydrate does not yield a pattern of X-ray diffraction lines, and in this sense may be said to have an amorphous character. By measurement of the heats of solution of the "X-ray amorphous" and crystalline monohydrates, the heat of transition has been found to be 6550 cal. mole^{-1}. Cobaltous chloride monohydrate prepared by vacuum dehydration appears to be microcrystalline. The heat of transition to the normal crystalline form is 1390 cal. mole^{-1}. These values are related to the surface areas of the vacuum dehydrated products.

INTRODUCTION

Kohlschütter and Nitschmann (5) have shown that when copper sulphate pentahydrate is dehydrated under vacuum, a product of monohydrate composition is obtained which does not yield a pattern of diffraction lines on X-ray examination. Hammel (3) obtained similar results for other dimetal sulphates, and Volmer and Seydel (8) for manganous oxalate dihydrate. For convenience, the term "X-ray amorphous" will be used to designate such products. These products have high energy contents with reference to the corresponding crystalline salts. From measurements of heats of solution, Frost, Moon, and Tompkins (1) found values of the order of 7000 cal. mole^{-1} for the heats of transition from the "X-ray amorphous" to the crystalline forms of copper sulphate monohydrate and zinc sulphate monohydrate.

Wheeler and Frost (9) have shown that the vacuum dehydration of magnesium sulphate heptahydrate results in the gradual loss of water to the monohydrate stage, the product showing no X-ray diffraction lines. This product is very stable, the characteristic monohydrate (kieserite) lines being formed only when the product is heated for two days at 130° C. They also found that on vacuum dehydration of cobaltous chloride hexahydrate, a gradual loss in weight occurred, the rate being rapid to the dihydrate stage followed by a much slower rate. It was not possible to characterize the final product by X-ray diffraction using the radiation available.

In the course of a more comprehensive study of the dehydration kinetics of these salts, and of other studies, it became desirable to have reasonably accurate information concerning the energetic character of the products of monohydrate composition obtained by vacuum dehydration, in reference to the normally occurring crystalline monohydrates. The purpose of this paper is to report the results obtained.

EXPERIMENTAL

The experimental method involved the comparison of the heats of solution of the crystalline monohydrates with those of the products of stoichiometric

[1]*Manuscript received November 18, 1955.*
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monohydrate composition obtained by vacuum dehydration. The calorimeter and general procedures were identical with those described in detail in the earlier work on copper and zinc sulphates (1).

Magnesium sulphate heptahydrate and cobaltous chloride hexahydrate, both of reagent grade, were recrystallized twice at room temperature, air dried, and screened, the "through 60 on 80 mesh" fractions being retained.

A series of mixtures of crystalline hydrates were prepared by dehydrating small weighed samples for various times at 100° C. in an Abderhalden apparatus containing fused calcium chloride as a desiccant. The percentage of water in each sample was calculated from the loss in weight. The heats of solution of these samples were determined and plotted against the water content, the value corresponding to the monohydrate composition being determined by extrapolation.

Vacuum dehydration to various water contents was carried out as follows. A weighing thimble containing a small weighed sample was placed in a tube which was connected to a vacuum line by means of a ground joint. The system was then evacuated (usually at 40° C.) for a sufficient time to give a product of the approximate composition desired. At the end of the evacuation, the pump was shut off, and dry air admitted to the system. The sample container was then quickly removed, capped, and weighed, the water content being determined by the weight loss. The heats of solution of the samples were determined, plotted against water content, and the value corresponding to the stoichiometric monohydrate composition determined by interpolation.

Samples of the magnesium salt were characterized by X-ray diffraction as required. It was not possible to obtain suitable diffraction patterns with the cobalt salt using the copper K_α radiation available.

RESULTS

Magnesium Sulphate

The results of determinations of the heats of solution of pure magnesium sulphate heptahydrate and of crystalline mixtures of hydrates, prepared by the dehydration of the heptahydrate in the Abderhalden apparatus, are given in Table I. In this, and the following tables, the percentage of water in a given

TABLE I

HEATS OF SOLUTION OF CRYSTALLINE HYDRATES OF MAGNESIUM SULPHATE

Expt. No.	Per cent water $= c$	Heat evolved, cal. gm.$^{-1}$	Heat of dilution, cal. gm.$^{-1}$ hydrated salt	J, cal. gm.$^{-1}$ hydrated salt	Temp., ° C.
1	51.16	−14.16	2.44	−11.72	26.92
2	51.16	−13.47	1.82	−11.65	26.04
3	51.16	−13.51	2.04	−11.47	26.08
4	30.26	49.26	2.78	52.0	26.62
5	30.19	51.71	2.59	54.3	27.00
6	20.66	76.54	3.27	79.8	26.25
7	20.00	78.82	2.56	81.4	26.23

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sample is denoted by c and the heat of solution to infinite dilution by J. Heats of dilution were obtained from the data of Lange and Streeck (6). The last column gives the temperature of the calorimeter at the instant of the salt addition. The results are plotted in Fig. 1, from which it will be seen that the

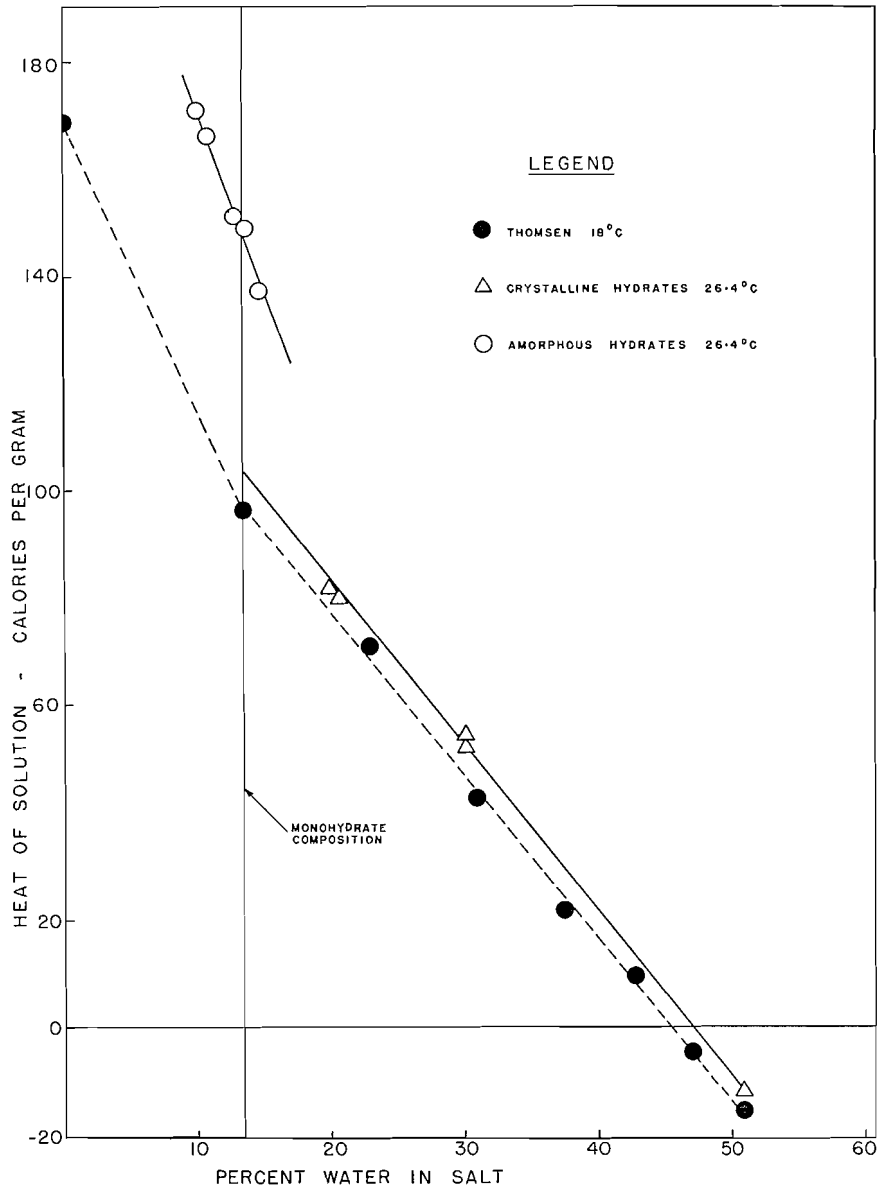

FIG. 1. Heats of solution to infinite dilution of crystalline and X-ray amorphous hydrates of magnesium sulphate.

heat of solution values for samples of water content between the heptahydrate and the monohydrate lie on a straight line.

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The equation of the best straight line, fitted to the points obtained by the method of least squares, is

$$J = 142.8 - 3.012\,c \quad (13.02 < c < 51.16)$$

from which the value of J corresponding to the percentage of water in the crystalline monohydrate ($c = 13.02\%$) is 103.6 cal. gm.$^{-1}$.

The results for the determinations of the heats of solution of samples dehydrated under vacuum are given in Table II and are also plotted in Fig. 1.

TABLE II

HEATS OF SOLUTION OF AMORPHOUS HYDRATES OF MAGNESIUM SULPHATE

Expt. No.	Per cent water = c	Heat evolved, cal. gm.$^{-1}$	Heat of dilution, cal. gm.$^{-1}$ hydrated salt	J, cal. gm.$^{-1}$ hydrated salt	Temp., ° C.
8	14.68	132.7	3.78	136.5	26.53
9	13.69	144.5	3.45	148.0	26.31
10	12.79	147.4	3.35	150.8	26.23
11	10.81	162.4	3.38	165.7	26.84
12	10.04	167.4	3.21	170.7	25.97

Although these samples varied somewhat in water content, none showed an X-ray diffraction pattern. It will be observed that the values lie on a straight line cutting the vertical line corresponding to the stoichiometric monohydrate composition.

The equation of the best straight line fitted to these values is

$$J = 243.1 - 7.077\,c \quad (10.04 < c < 13.69)$$

from which J is 150.9 cal. gm.$^{-1}$ for the dehydration product having the stoichiometric monohydrate composition.

TABLE III

HEATS OF SOLUTION OF CRYSTALLINE AND VACUUM DEHYDRATED HYDRATES OF COBALT, CHLORIDE

Expt. No.	Method of dehydration	Time of salt addition after evacuation, min.	Sample wt., gm.	Per cent water = c	Heat evolved, cal. gm.$^{-1}$	Temp., ° C.
20	—	—	2.3511	45.43	−8.32	25.93
21	Abderhalden	—	0.5188	11.99	94.08	25.46
22	Abderhalden	—	0.9115	7.69	110.4	26.45
23	Vacuum	359	0.5514	16.64	78.6	26.62
24	Vacuum	10	0.3988	16.92	81.1	25.73
25	Vacuum	10	0.3529	16.41	82.6	25.26
26	Vacuum	278	0.4820	16.92	78.6	25.92
27	Vacuum	122	0.4648	16.41	80.1	25.76
28	Vacuum	10.5	0.5944	18.50	71.0	26.30
29	Vacuum	10	0.3788	11.22	105.4	25.23
30	Vacuum	10	0.6225	8.62	119.3	25.94
31	Vacuum	130	0.4149	8.62	119.2	25.58
32	Vacuum	10	0.4995	3.09	147.7	25.51

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The difference in these values of J is 47.3 cal. gm.$^{-1}$. Hence for:

$$MgSO_4.H_2O(\text{X-ray amorphous}) \rightarrow MgSO_4.H_2O(\text{crystalline}),$$
$$\Delta H_{300°K.} = -6550 \text{ cal. mole}^{-1}$$

with a probable uncertainty of ± 100 cal.

Cobaltous Chloride

The heat of solution results for both crystalline and vacuum dehydrated samples are given in Table III and are plotted in Fig. 2. Unfortunately no heat

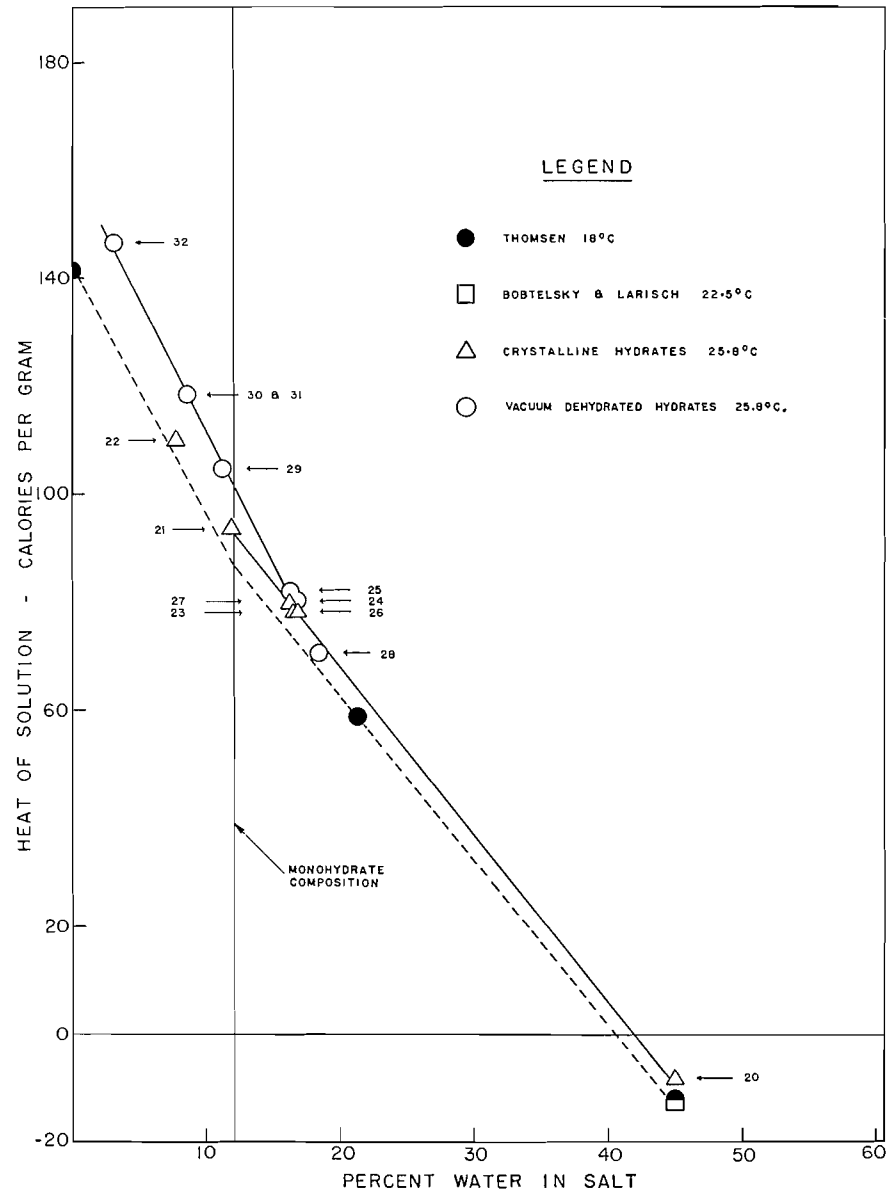

FIG. 2. Heats of solution of crystalline and vacuum dehydrated hydrates of cobalt chloride.

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of dilution data are available for this salt. It has been thought desirable, therefore, to tabulate the sample weights used. The amount of water in the calorimeter in each determination was 591.6 ± 0.2 gm.

The results obtained in Expt. 20 refer to the crystalline hexahydrate. In Expt. 21 dehydration was carried out to the crystalline monohydrate stage. Expt. 23 is a vacuum dehydration in which nearly six hours elapsed between the end of dehydration and the introduction of the sample into the calorimeter. It was observed that the heat of solution value for this vacuum dehydrated product fell on the straight line joining the values obtained for the crystalline hexahydrate and the crystalline monohydrate. In view of this result, it was first thought that a high energy intermediate was not formed on vacuum dehydration. It was then considered possible that the product had reverted to the normal crystalline form during the period which elapsed between the end of the dehydration process and the introduction of the sample into the calorimeter. Accordingly Expts. 24 and 25 were carried out in which the heat of solution determinations were made as soon as possible after evacuation. These were found to give slightly higher values than Expts. 26 and 27 in which dehydration was carried out to approximately the same water content as before, but a considerable time allowed to elapse between the dehydration and calorimetric procedures.

Expts. 29, 30, and 32 are vacuum dehydrations carried to lower water contents, the samples being introduced into the calorimeter within 10 min. after dehydration. The heat of solution values lie on the upper straight line of Fig. 2. It is interesting to note that the heat of solution value obtained in Expt. 30 is the same as that obtained from a sample of the same product taken two hours later, reported as Expt. 31. This indicates that the high energy intermediate is more stable for samples having a percentage of water less than that corresponding to the monohydrate. Expt. 28 is of interest in that, although the dehydration was carried out under vacuum and the sample transferred to the calorimeter quickly, the heat of solution value lies slightly below the line drawn through the values obtained for the crystalline samples. This result cannot be accounted for by experimental error and suggests that some phase transition occurs just prior to the formation of the monohydrate phase. Further exploration of this region would be of interest.

The best straight line, calculated by the method of least squares, for the crystalline hydrates, from the data of Expts. 20, 21, 23, 26, and 27 is:

$$J' = 130.1 - 3.048\,c \quad (11.99 < c < 45.43)$$

where J' is the experimental value of the heat of solution uncorrected for the heat of dilution. The value of J' corresponding to the percentage of water in the monohydrate ($c = 12.18\%$) is 93.0 cal. gm.$^{-1}$.

The equation of the best straight line for the heats of solution of the vacuum dehydrated products of Expts. 24, 25, 29, 30, and 32 was found to be

$$J' = 161.5 - 4.848\,c \quad (3.09 < c < 18.50)$$

from which the value of J' corresponding to the monohydrate composition is 102.4 cal. gm.$^{-1}$.

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The difference in heat of solution between the vacuum dehydrated and crystalline monohydrates is therefore 9.4 cal. gm.$^{-1}$, or for the change in state,

$$CoCl_2.H_2O(\text{vacuum dehydrated}) \rightarrow CoCl_2.H_2O(\text{crystalline}),$$
$$\Delta H_{300°K.} = -1390 \text{ cal. mole}^{-1}.$$

This value is to be regarded as somewhat approximate in that the interval between evacuation and placing the sample in the calorimeter (during which some crystallization may have occurred in samples of higher water content) is arbitrary.

COMMENT

The value obtained in the foregoing for the heat of transition of X-ray amorphous magnesium sulphate monohydrate to the corresponding crystalline form is comparable to those previously reported for the copper and zinc sulphate monohydrates (1). The value obtained for the cobalt salt is significantly lower. It is unfortunate that characterization of the product obtained on vacuum dehydration could not be made by X-ray diffraction. However, such results would be of doubtful value in view of the rapidity of crystallization, unless a technique could be devised whereby dehydration could be carried out in the X-ray camera itself.

The surface area of magnesium sulphate monohydrate prepared by vacuum dehydration is approximately 8 meters^2 gm.$^{-1}$; that of cobalt chloride monohydrate is 35.9 meters^2 gm.$^{-1}$. Both of these values were determined by argon adsorption at 78° K. (7). The ratio of the heat of transition per gram to the surface area of the vacuum dehydrated product is 5.9 cal. meters^{-2} for the magnesium salt, and 0.26 cal. meters^{-2} for the cobalt salt.

Giauque (2) has reported a value of 22.2 cal. gm.$^{-1}$ for the heat of transition of magnesium oxide from a finely divided crystalline to the normal macrocrystalline form. Jura and Garland (4) have reported the surface area of finely divided magnesium oxide prepared in a similar manner to that of Giauque to be 86 meters^2 gm.$^{-1}$. The experimental evidence indicates that the heat of transition is wholly due to the difference in surface area between the finely divided and normal crystalline forms. The ratio of the heat of transition to surface area is 0.26 cal. meters^{-2}.

The identical agreement of this value with the ratio obtained for cobalt chloride is undoubtedly fortuitous in view of the uncertainties involved. Nevertheless, the values of these ratios are comparable, and suggest that the product of vacuum dehydration of cobaltous chloride hexahydrate is microcrystalline and that the difference in heat of solution between the normal crystalline monohydrate and that formed by vacuum dehydration results, as with magnesium oxide, from the difference in crystal dimensions only. If this view is correct, it must be assumed that the microcrystals are accessible to the gas used in determining the surface area by the usual adsorption methods, or, in other words, that the surface area values have the same significance for cobaltous chloride monohydrate as for magnesium oxide.

The vacuum dehydration products of both cobaltous chloride hexahydrate and magnesium sulphate heptahydrate have large internal surfaces resulting

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from capillary formation (7). It is probable that these capillaries are formed as the lattice contracts with the movement of the dehydration interfaces along preferred planes. In terms of the foregoing interpretation, it must be assumed that, for the cobalt salt, this lattice contraction is associated with the formation of loosely packed aggregates of microcrystals differing from crystals of the normal monohydrate in dimensions only.

For magnesium sulphate monohydrate, prepared by vacuum dehydration, the ratio of heat of transition to surface area is very much higher. It is possible that this material also consists of microcrystals. If this is so, however, the dimensions of these must be below the limit required for X-ray diffraction (about 100 Å). It is possible that these crystallites are packed in localized regions and that the adsorption surface area gives, not the area of the microcrystals, but the area resulting from the internal capillary structure. Consequently, the ratio of heat of transition to surface area would have a very different meaning than that just considered.

It is of interest, however, to point out another aspect of the magnesium sulphate dehydration. The crystalline monohydrate (kieserite) is known to be very stable and does not lose water at temperatures below about 200° C. under atmospheric pressure. It has been suggested, on this basis, that the water molecule does not exist as an entity in the kieserite lattice. However, the data given in Table II show that a loss in weight, corresponding to water contents well below the monohydrate stage, takes place quite readily during vacuum dehydration at 40° C.

These products have been found to give the characteristic kieserite diffraction lines when heated for two or three days at about 130° C. It is possible, therefore, that vacuum dehydration of the heptahydrate results in the formation of an intermediate, which under proper conditions crystallizes into the kieserite lattice. The measured heat of transition would therefore be the energy release accompanying crystallization from the intermediate, and not that associated solely with change in surface.

It is intended to present other data pertinent to the nature of X-ray amorphous dehydration products in a later paper.

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THE LOW PRESSURE DEHYDRATION OF MAGNESIUM SULPHATE HEPTAHYDRATE AND COBALTOUS CHLORIDE HEXAHYDRATE[1]

By R. W. Ford[2] and G. B. Frost

ABSTRACT

Rates of dehydration under vacuum, and at a series of controlled water vapor pressures, have been carried out for powdered samples of magnesium sulphate heptahydrate and of cobaltous chloride hexahydrate. It has been found for the magnesium salt that as the pressures are increased, the rate at first drops rapidly, this decrease being followed by a period of acceleration which is followed in turn by a decline. The curves are similar to those previously reported for copper sulphate pentahydrate, but the changes occur over a much wider range of water vapor pressures. In the dehydration of cobaltous chloride hexahydrate the initial drop in rate with increase in water vapor pressure is not observed. The results are interpreted in terms of the crystallization of intermediate products in the presence of adsorbed water.

INTRODUCTION

Recently, Wheeler and Frost (8) have reported the results of a survey of the dehydration kinetics of a number of hydrated salts. It has been shown that the rate of dehydration is markedly affected by the pressure of water vapor at the reaction interface, acceleration in rate being frequently observed over certain pressure ranges. Some hydrated salts on low pressure dehydration yield products which do not give diffraction lines on X-ray examination and therefore have no evident crystalline structure. For others the end products are crystalline. A more detailed study of the rates of dehydration at a series of water vapor pressures of magnesium sulphate heptahydrate, and of cobaltous chloride hexahydrate, has revealed some interesting points, both of similarity and contrast, in these respects. The purpose of the present paper is to report these findings.

EXPERIMENTAL METHOD

Determinations of rates of dehydration under vacuum, and also at externally controlled and constant pressures of water vapor, have been carried out. The apparatus and experimental method differed in no important respect from that used by Frost and Campbell (2) in a comparable study of the dehydration kinetics of copper sulphate pentahydrate. Rates of dehydration were measured by reading the extension of a quartz spiral from which small powdered samples were suspended. Water vapor, at pressures below 4.58 mm., was obtained by maintaining ice crystals, deposited on glass wool, at suitable low temperatures. Water vapor at higher pressures was obtained by first evacuating the system containing ice crystals at low temperatures, and then allowing these to melt by surrounding the container with a temperature-controlled water bath through which cold water could be circulated as needed. It was found that the temperature could be controlled to $\pm 0.02°$ C.

[1]*Manuscript received November 18, 1955.*
Contribution from the Department of Chemistry, Queen's University, Kingston, Ontario.
[2]*Present address: Graduate student in Chemistry, McMaster University, Hamilton, Ontario.*

In rate experiments carried out in the presence of water vapor, samples were nucleated by dehydrating under vacuum for two or three minutes during which period readings were taken. The spiral case was then shut off from the vacuum system and exposed to water vapor at the desired pressure, readings of spiral extensions being continued for the duration of the experiment. X-ray powder photographs were made of the dehydration products of magnesium sulphate heptahydrate. Unfortunately this was not possible for the cobalt salt since the copper K_α radiation used was strongly absorbed, resulting in fluorescent radiation.

RESULTS

Magnesium Sulphate Heptahydrate

The dehydration of magnesium sulphate heptahydrate was studied at 40°, 50°, and 60° C. and over a range of water vapor pressures from zero to approximately 18 mm. Hg at each temperature. At 40° C., eight experiments were conducted, curves showing loss in weight in milligrams versus time in minutes being shown in Fig. 1.

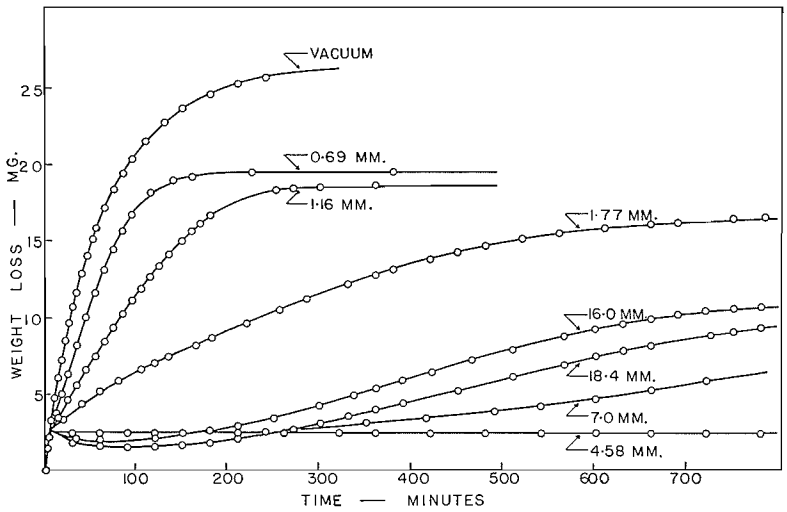

FIG. 1. The change in weight loss of fine crystal aggregates of magnesium sulphate heptahydrate at a series of constant water vapor pressures at 40° C.

These curves fall into three groups. Under vacuum, and at water vapor pressures of 0.69, 1.16, and 1.77 mm., the curves show a smooth and gradual decrease in rate as the dehydration progresses. Also the initial slope of each curve decreases with increasing pressure. The composition of the products varied from the monohydrate in the vacuum dehydration to approximately the tetrahydrate stage in the dehydration at 1.77 mm. None of these products diffracted X-rays.

The curve obtained at 4.58 mm. was unique in that no decomposition was apparent after the initial nucleation period.

All of the experiments at pressures of 7 mm., or higher, gave curves of a sigmoid character; that is, following nucleation, an induction period set in

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during which no weight loss was observed. During this period, a slight gain in weight was sometimes noted, which was probably due to the adsorption of water on the outer dehydrated layer. This period was followed by another during which the rate of decomposition was almost constant with time, before gradually decreasing as the reaction neared completion. It will be seen that for the curves obtained at 7.0 mm., 16.0 mm., and 18.4 mm., the slopes of these nearly linear portions first increase with increasing pressure and then decline. The end products corresponding to these sigmoid type curves were crystalline, clearly defined diffraction patterns of tetrahydrate lines being obtained.

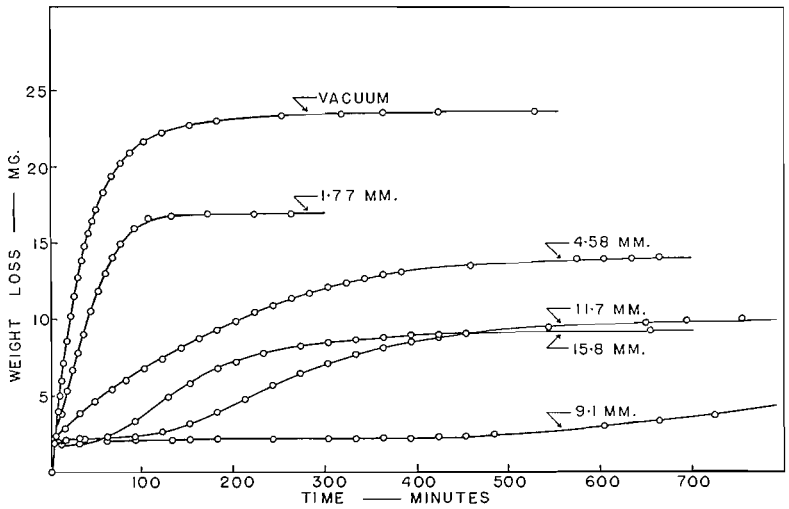

FIG. 2. The change in weight loss of fine crystal aggregates of magnesium sulphate heptahydrate at a series of constant water vapor pressures at 50° C.

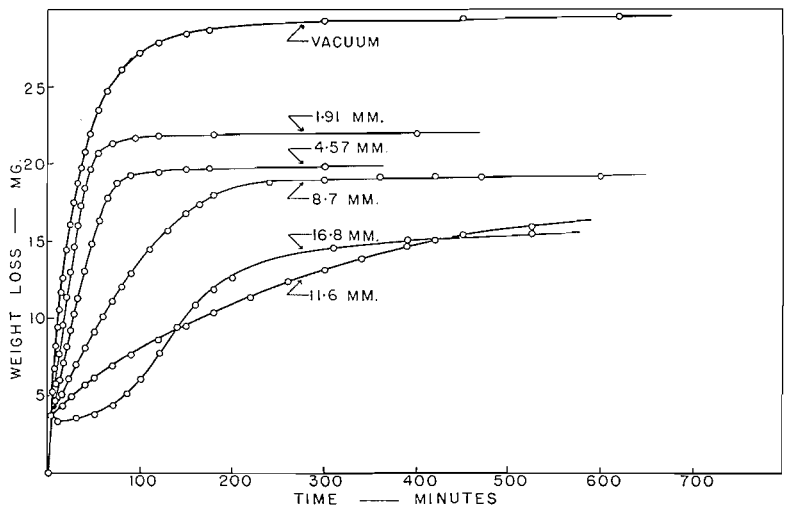

FIG. 3. The change in weight loss of fine crystal aggregates of magnesium sulphate heptahydrate at a series of constant water vapor pressures at 60° C.

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Curves obtained from dehydrations carried out at 50° C. and 60° C. are shown in Figs. 2 and 3 and are similar in character to those just described.

It is evident from all of these plots that the duration of the induction periods decreases as either the pressure or the temperature is increased. This effect of pressure is shown most clearly in the group of curves obtained at 50° C.

The change in rate of dehydration with water vapor pressure per decigram of material is shown in Fig. 4. These rates have been obtained by the method used by Frost and Campbell (2) in their study of the dehydration of copper

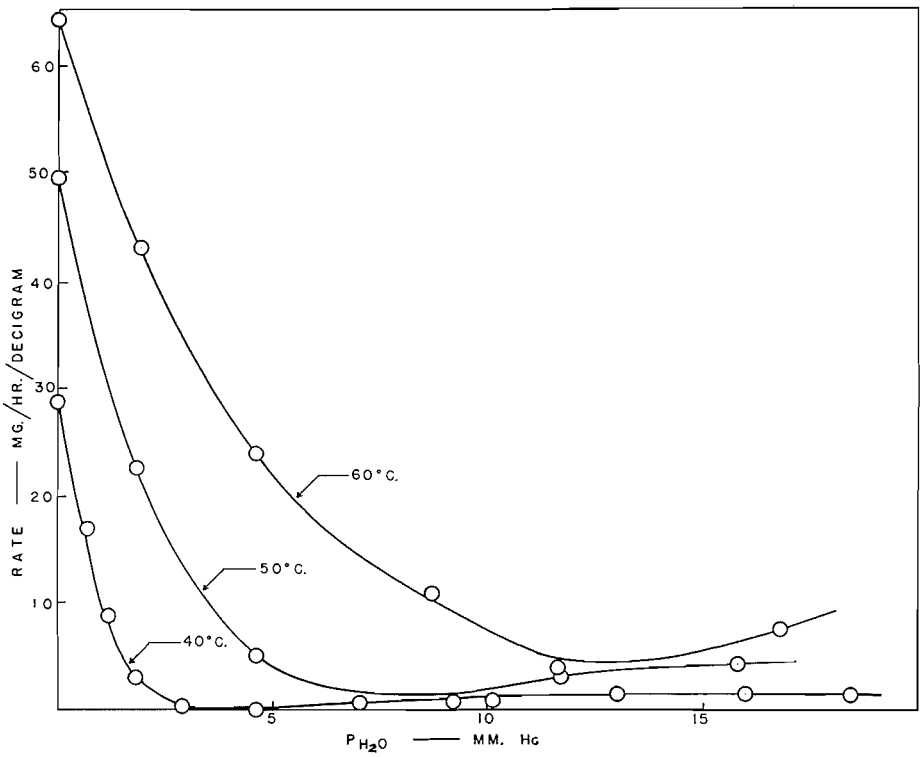

FIG. 4. The dependence of over-all dehydration rate upon water vapor pressure for magnesium sulphate heptahydrate.

sulphate pentahydrate. Essentially, the rates compared correspond to the slopes of the initial (nearly linear) portions of the curves showing a gradual decline in rate at low pressures, and to the slopes of the nearly linear portions following the induction period for the curves which are sigmoid in character.

At each of the three temperatures, the rate is seen to decrease fairly rapidly with increasing water vapor pressure until a minimum is reached, after which the rate increases. At 40° C., and 50° C., the rates decline again at higher pressure. This decline could not be observed at 60° C. since sufficiently high pressures could not be conveniently obtained by the experimental method used.

The curves shown in Fig. 4 are very similar to these reported by Frost and Campbell for copper sulphate pentahydrate, and by Topley and Smith (5) and

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by Volmer and Seydel (6) for manganous oxalate dihydrate, except that the pressure at which the minimum in rate occurs is very much higher. The minimum occurs at higher pressures as the temperature is increased.

Cobaltous Chloride Hexahydrate

Studies of the rate of dehydration of this salt were carried out at 30° C. and 40° C. at water vapor pressures ranging from zero to approximately 18 mm. Hg.

The dehydration curves obtained at these two temperatures are shown in Figs. 5 and 6 respectively. The end product of the vacuum dehydrations, which were carried out for 30 hr., was a product of somewhat lower water content

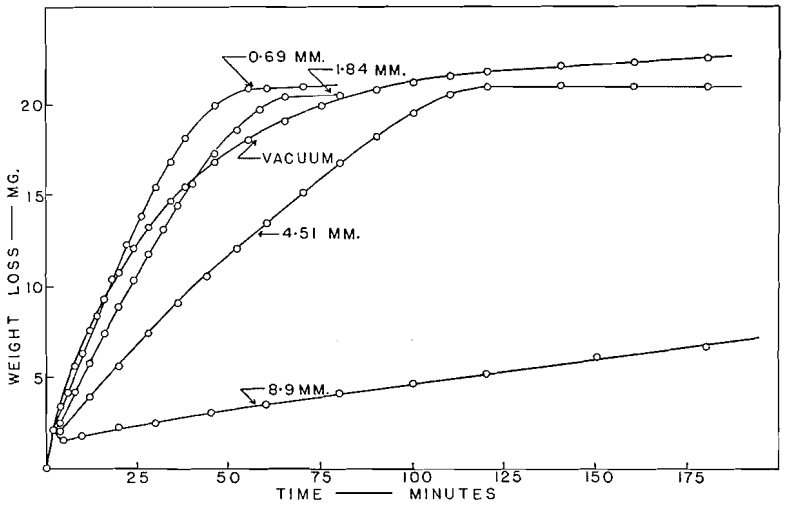

FIG. 5. The change in weight loss of cobalt chloride hexahydrate at a series of constant water vapor pressures at 30° C.

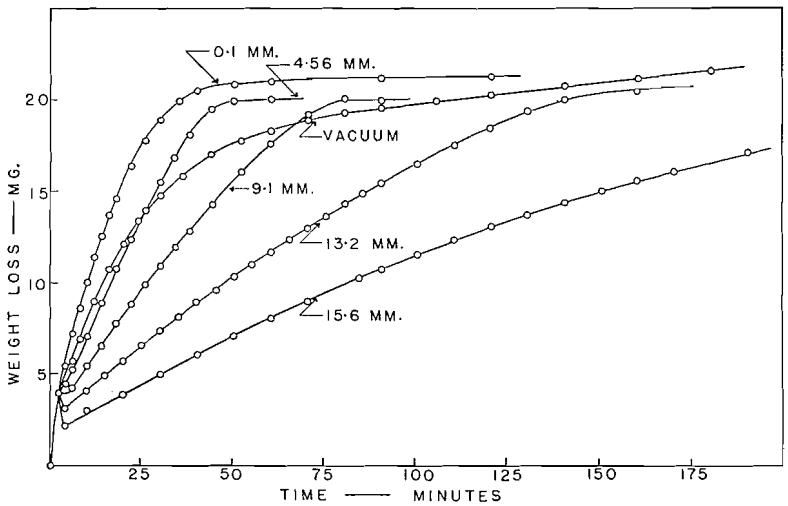

FIG. 6. The change in weight loss of cobalt chloride hexahydrate at a series of constant water vapor pressures at 40° C.

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than the stoichiometric monohydrate composition. For the other determinations, the rate of decomposition became very slow when the dihydrate stage was reached. Control experiments showed that no significant amount of hydrogen chloride was formed in any of these dehydrations (4).

These curves show several interesting features in comparison with those obtained for magnesium sulphate heptahydrate. The curves obtained for vacuum dehydrations are somewhat similar. However, when water vapor at low pressure is admitted to the system, the cobalt salt shows quite different properties. Whereas with the magnesium salt, the initial slopes of the weight-loss curves decrease with increasing pressure, the slopes of the curves obtained with cobalt chloride hexahydrate initially increase with increasing pressure up to a limiting value, after which the slopes decrease, and then only gradually. Curves of a sigmoid character were not obtained at any pressure. At higher pressures, a slight gain in weight was observed following the nucleation period, but this effect was probably due to the adsorption of water vapor on the dehydrated surface and bore no resemblance to the induction periods observed for magnesium sulphate heptahydrate.

Rate values, calculated per decigram of sample, and obtained from the nearly linear portions of the weight-loss curves, are shown plotted against water vapor pressure in Fig. 7.

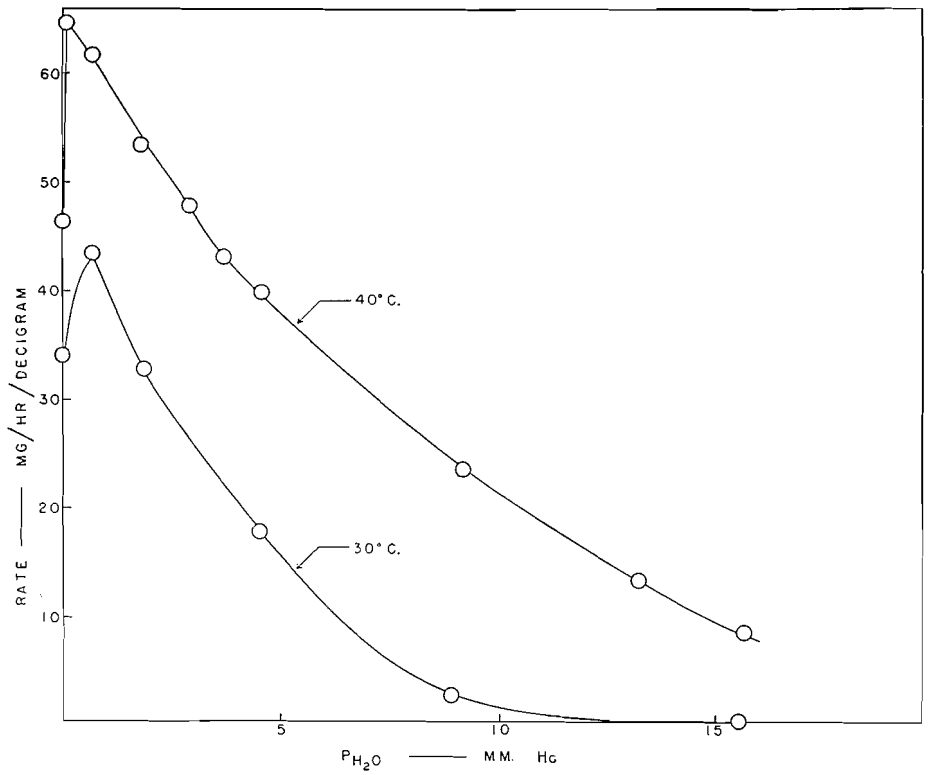

FIG. 7. The dependence of over-all dehydration rate upon water vapor pressure for cobalt chloride hexahydrate.

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DISCUSSION

The dependence of the rate of dehydration of magnesium sulphate heptahydrate upon water vapor pressure has been found to be similar to that which has been reported for copper sulphate pentahydrate except that the minimum in rate occurs in a very much higher range of pressure. It would appear reasonable therefore to give the same interpretation of these curves as has been done for the copper sulphate pentahydrate dehydration (2). Under vacuum, the parent lattice breaks down into a state of monohydrate composition which does not yield a pattern of X-ray diffraction lines. It has been shown elsewhere that this material is very stable, and that the heat of crystallization is approximately 6500 cal. per formula wt. (3). Data regarding its surface area and capillary structure have been reported (4). At water vapor pressures below those corresponding to the minima in rates shown in Fig. 4, a material is formed which likewise does not diffract X-rays, but the rate of dehydration becomes very slow after the approximate stoichiometric composition of the tetrahydrate is reached.

At pressures higher than those corresponding to the minima in rates (or therefore those for which the weight loss curves show induction periods) the end product of dehydration is crystalline tetrahydrate. In these experiments a layer of amorphous material is formed in the nucleation stage of dehydration. Upon exposure to water vapor the induction period immediately sets in, which may be interpreted as a period during which crystallization of the X-ray amorphous transition layer takes place under the influence of adsorbed water. This effect occurs over small ranges of pressure and appears to be specifically due to water. Experiments have been carried out in order to ascertain if methyl or ethyl alcohol have any effect in accelerating the rate of these dehydrations, but with negative results. Upon the occurrence of crystallization the escape of water molecules is facilitated, giving rise to the nearly linear increase in the loss-in-weight curves following the induction periods. The final decline in rate may be ascribed to the impedance of this crystalline layer. The occurrence of a zero rate at approximately 4.58 mm. in the dehydration at 40° C. is of interest. It is probable that this is a very long induction period, and if carried farther would resemble the dehydration of 9.1 mm. at 50° C. shown in Fig. 2.

The relatively high pressure at which the minimum in rate occurs has been related elsewhere to the low adsorptive capacity and the capillary structure of the X-ray amorphous material (4). The observed shift of the minimum toward higher pressures by increase in temperature would be expected if it is assumed that a definite quantity of adsorbed water is required to induce crystallization of the amorphous material. Since the adsorption of water will be lowered by rise in temperature, it follows that as the temperature is increased, a higher water vapor pressure external to the interface will be required to provide the necessary quantity of water in the reaction zone.

The dependence of the rate of dehydration of cobaltous chloride hexahydrate upon water vapor pressure is very similar to that observed for the dehydration of chrome alum by Cooper and Garner (1) who made microscopic measurements on the rate of growth of nuclei on single crystals. They assumed the

formation of a transition layer (probably microcrystalline) at the reaction interface and explained the maximum in rate observed at low pressure as being due to a decrease in the thickness of this transition layer as a consequence of the development of macrocrystals of the product. X-ray powder photographs, made in this laboratory, of the vacuum dehydration product of chrome alum show a definite diffraction pattern. Although X-ray diffraction data for the cobalt salt are lacking, observations reported by Jamieson and Frost (3) during determinations of the heat of solution of the vacuum dehydrated product indicate that vacuum dehydration results in a microcrystalline product of high internal surface, the formation of macrocrystals occurring readily.

The group of loss-in-weight versus time curves obtained for this salt are similar to the group of curves following the long induction periods observed in the dehydration of magnesium sulphate heptahydrate or copper sulphate pentahydrate, in that the over-all dehydration rate at first increases with water vapor pressure, and then declines. The absence of observable induction periods in the dehydration of cobalt chloride hexahydrate suggests that the processes assumed to occur during them (i.e. crystallization of amorphous material) either do not occur at all, or take place at extremely low pressures.

It is possible that a state corresponding to the X-ray amorphous state of magnesium sulphate monohydrate is formed as a transitory step as the primary lattice breaks down, but that crystallization occurs immediately. If the presence of water is a necessary factor, this crystallization must take place merely as water molecules from the reaction zone pass through the transition layer. There will result a mesh of microcrystals interspersed with capillaries formed by lattice contraction, the surface properties of which have been described elsewhere (4).

With increase in water vapor pressure external to the reaction zone, further adsorption will occur, resulting in crystal growth, and further contraction in volume, resulting in larger capillaries. In consequence, the more rapid escape of water molecules from the reaction interface will be facilitated, and the observed increase in rate accounted for. The decline in rate following the observed maximum may, as before, be ascribed to the impedance of the growing crystalline layer. This crystalline layer appears to have the composition of the dihydrate. It has been pointed out elsewhere (8) that the rate of dehydration under vacuum proceeds fairly rapidly to the dihydrate stage, followed by monohydrate formation at a slower rate. It appears that this second rate becomes very much slower in the presence of water vapor at low pressures.

It should be noted that the maximum in rate is displaced in the direction of lower pressure with temperature increase, whereas the reverse is true for magnesium sulphate heptahydrate. It has been pointed out that if water plays any significant role in the formation of crystalline dehydration products of cobalt chloride hexahydrate, the quantities required are very small. Any slight adsorption of water will of course decrease with temperature rise. However, it has been shown (3) that the product formed on vacuum dehydration forms

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macrocrystals very readily. It is probable that this crystallization rate increases with temperature and is therefore more significant than the adsorption factor.

In this study, and in other studies of the rates of dehydration of hydrated salts which have been reported, there seems to be a common over-all pattern of the sequence of changes occurring. The point of real interest is the mechanism whereby these changes occur in the presence of adsorbed water, and the variation in the range of pressures of water vapor over which this sequence of changes is observed for different salts. It would be of interest to attempt to correlate these findings with data concerning the crystallographic changes involved. Although some suggestive information is available concerning these crystal structures (7), our knowledge is not as yet sufficiently comprehensive for this purpose.

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THE INFLUENCE OF ALKALI ON THE OXIDATION OF TETRALIN[1]

By K. U. Ingold

ABSTRACT

Strong alkalies are powerful catalysts for the initial oxidation of tetralin but their catalytic activity is rapidly replaced by an inhibiting action which makes oxidation of more than 5% of the tetralin an exceedingly slow process. Inhibition is due to the base catalyzed enolization and oxidation of the initial product, 1-tetralone, to various naphtholic compounds. Ring scission yields β-2-carboxyphenylpropionic acid. The rate shows a certain periodicity which may be due to the reaction proceeding by a series of consecutive autocatalytic steps.

INTRODUCTION

Not much is known about the influence of alkali on the oxidation of liquid hydrocarbons (4) but some recent work in these laboratories has shown that the rate of oxidative discoloration of lubricating oils is markedly reduced by the addition of alkali (17). The present work was started in the hope of elucidating this effect by the examination of a less complex system.

Tetralin was chosen for study as a large amount of work has been done on its catalyzed, uncatalyzed, and inhibited oxidation (1, 6–10, 13, 15, 16). The general features of its oxidation are now fairly well understood. In the uncatalyzed reaction tetralin is autoxidized first to a fairly stable hydroperoxide which subsequently breaks down to give a variety of products (16).

EXPERIMENTAL

The general design of the apparatus was the same as that described by Cooper and Melville (3). The manostat, which was used to follow the oxygen uptake at constant pressure, was immersed in a water bath at 34.0° C. The pyrex reaction vessel was connected to the manostat by way of a silicone greased cone and socket and a flexible glass spiral. The cone had a short projection on it that prevented any tetralin which distilled up to the grease during the course of a reaction from returning to the reactants. The reaction vessel was immersed in an oil bath at 119.0° C. and was shaken at 250 cycles/min. Tetralin was added to it from a constant volume pipette (3) which delivered 2.5 ml. The reaction vessel was cleaned by washing with benzene, alcohol, and distilled water, followed by heating to the softening point of glass in a stream of dry air in order to burn out any insoluble residue.

Infrared spectra were taken with a Model 21 Perkin–Elmer infrared spectrophotometer.

PURIFICATION OF TETRALIN

Commercial tetralin was shaken repeatedly with concentrated sulphuric acid until there was no discoloration. It was then washed with water, dilute alkali, and again with water. After being dried with $CaSO_4$ it was run through

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an alumina column and distilled twice under vacuum from sodium through a 2 ft. column packed with Dixon gauze rings (2). It was stored under an atmosphere of pure nitrogen.

Infrared analysis showed the purified tetralin to contain less than 0.05% of hydroperoxide, less than 0.1% of ketone, and only a very small amount of 1,2-dihydronaphthalene. The refractive index was 1.538_8 (n_{25}^{D}).

RESULTS

Kinetic Data

All the work reported in this paper was done at 119.0° C. with 2.5 ml. samples of tetralin.

Table I gives some data on the effect of various alkaline additives on the maximum rate of oxidation of tetralin (r_{max}, given in ml. O_2 at S.T.P./liter

TABLE I

EFFECT OF ALKALI ON THE OXIDATION OF TETRALIN

Additive	r_{max}	t_{max}	t_1	t_3	t_5	t_6	t_{10}	t_{20}
None	12.9	2550	560	990	1295	1425	1865	2855
Strong alkali	20.0	275	265	590	1630	3270	11800	23000 (t_{12})
0.5 gm. Na_3PO_4	9.9	75	160	565	885	1035	1565	2875
	9.8	1700						
1.0 gm. $C_6H_4(CO_2)_2K_2$	10.9	2100	550	950	1240	1380	1870	—
0.1 gm. Na_3PO_4	12.4	2500	520	970	1275	1415	1875	2950
2.0 gm. Na_3PO_4	18.1	75	75	415	1200	1690	3445	7400
Clear liquid from "alkali" run	10.2	2300	430	890	1210	1360	1910	3200

tetralin/sec.), on the time at which the maximum rate is reached (t_{max}, sec.), and on the times to various percentages of oxidation (t_1, t_3, etc., calculated for 1 mole O_2/mole tetralin). All data given are averages of at least two experiments. The run without additives, called hereafter the "normal" run, was an average of about 20 runs, none of which differed by more than 5% from the mean. In the presence of strong alkali, although the time taken to reach a given amount of oxidation was reproducible to within 5 or 10%, the maximum rate was of such short duration that it may be in error by 20%. Within the experimental error the same rates and times were obtained with 0.1–0.5 gm. NaOH, 0.5 gm. of sodium metal, and 0.5 gm. of a 10% Na – 90% Pb alloy. These runs with strong alkali are called hereafter "alkali" runs. For contrast the "normal" and "alkali" oxidation curves are shown in Fig. 1. It can be seen that the initial catalytic activity of the alkali is rapidly replaced by a strong inhibiting action. In addition to the very sharp maximum at 275 sec., there are two or more subsidiary maxima, the most noticeable of which occur at about 650 and 1300 sec.

The "normal" reaction went through the color sequence from light yellow (10% oxidation) to canary yellow (35%) and finally to a viscous reddish-orange oil. Oxidation in the presence of strong alkali gave a fine suspension of solid particles which went through a large range of colors. At 5% oxidation the color was yellow, at 7% brown, then greenish-brown, green (9%), dirty green, yellow,

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and finally reddish-orange (10–12%). If the suspension was removed by centrifuging or by extraction with water, the liquid remained colorless until about 10% oxidation; it then showed a faint reddish-yellow color.

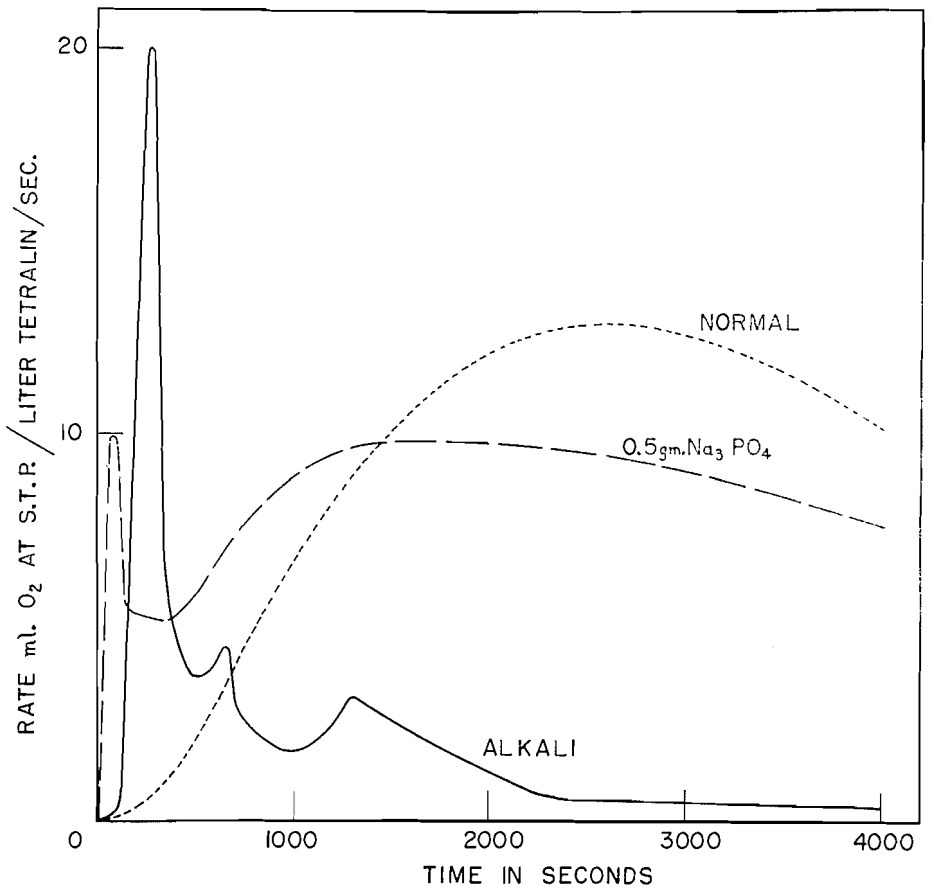

FIG. 1. The rates of oxidation of tetralin for "normal", "alkali", and Na_3PO_4 reaction.

The effect of moderate amounts of weak alkali, e.g. 0.5 gm. of dehydrated Na_3PO_4, was to give a combination of the "normal" and the "alkali" oxidation curves. The curve showed two maxima, the first near the beginning of the reaction and the second at about 12% oxidation (see Table I and Fig. 1). The liquid was a faint reddish-yellow at 30% oxidation.

Small amounts of weak alkali, e.g. 0.1 gm. of Na_3PO_4, or larger amounts of very weak alkali, e.g. 1.0 gm. of dipotassium phthalate, merely lowered the maximum rate of an otherwise "normal" reaction. The liquid was canary yellow at 25% oxidation.

Large amounts of weak alkali, e.g. 2 gm. of Na_3PO_4, gave an oxidation curve of the "alkali" type. However, the rate after 6% oxidation did not decrease sharply, but steadied down to a value of about 3.0 after 600 sec. The liquid was reddish-yellow at 25% oxidation.

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A 5% oxidized "alkali" run (rate = 0.4) was centrifuged and all the solids removed. Measurements were then made on the further oxidation of the clear liquid (Table I). The reaction was of the "normal" type with only slight inhibition. The liquid became light yellow in color. The solid portion of the "alkali" run was washed with tetralin, dried, and then added to a fresh sample of tetralin. The rate remained low (0.38) and fairly constant to 12,000 sec. (t_1 = 4,800, t_3 = 11,700 sec.). The liquid remained colorless.

The addition of 0.3 gm. NaOH to a "normal" run after 1500 sec. (rate = 10.0) produced for the first 50 sec. an apparent negative rate due to the evolution of steam. After 400 sec. the rate reached its maximum value (3.9) and then fell rapidly to a low value characteristic of an "alkali" reaction. The pale yellow color of the "normal" run was changed to a pale pink. Na_3PO_4 would also convert the yellow color of a "normal" run to the pale pink color characteristic of an "alkali" run.

It is known from the work of Hock and Susemihl (11) that 1-tetralone is a major product of the "alkali" reaction. The influence of pure 1-tetralone on the oxidation of tetralin was therefore studied.

The addition of 0.2 ml. of 1-tetralone had only a slight effect on the reaction. The oxidation times were the same as those of a "normal" run but the maximum rate was a little lower (Table II). A rather larger inhibition was obtained by the addition of 0.2 ml. of a sample of 1-tetralone which had been 3% oxidized.

TABLE II

EFFECT OF KETONES ON THE OXIDATION OF TETRALIN

Additive	r_{max}	t_{max}	t_1	t_3	t_5	t_{10}	t_{20}
0.2 ml. 1-tetralone	12.2	2600	555	980	1285	1895	2950
As above, 3% oxidized	10.1	3900	590	1190	1625	2430	3760
0.5 ml. 1-tetralone + 0.3 gm. NaOH	4.6	2250	950	1630	2190	3740	—
0.2 ml. *n*-valerophenone	12.6	150	110	330	540	1045	2105

1-Tetralone autoxidized very slowly compared with tetralin, but in the presence of alkali it was oxidized to a dark viscous oil with extreme rapidity, the rate reaching 78.0 in 300 sec. A large amount of water was evolved and the reaction mixture went rapidly through the color sequence blue-green, brown-green, brown, purple, cherry red, and finally black and opaque. In contrast a mixture of 1-tetralone, tetralin, and alkali gave a "normal" type oxidation curve with a very low maximum rate (Table II). The liquid became cherry red in color.

For comparison with the effects produced by 1-tetralone some experiments were done adding other compounds containing a carbonyl group adjacent to a benzene ring.

The addition of 0.1 ml. of acetophenone gave a slightly lower maximum rate than a "normal" reaction, but the same amount had no effect on the reaction in the presence of strong alkali.

The addition of 0.2 ml. of *n*-valerophenone ($C_6H_5.CO(CH_2)_3CH_3$) strongly catalyzed the oxidation of tetralin (Table II). Within the first 200 sec. the

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rate rose to the maximum value characteristic of the "normal" rate of oxidation. It then decreased in accordance with first order kinetics until 20% of the tetralin had been oxidized. Beyond 20% the rate decreased more rapidly.

n-Valerophenone autoxidized very slowly ($r = 0.4$ after one hour, 0.45% oxidized); its rate of oxidation at 119° C. was unaffected by alkali. The addition of *n*-valerophenone and alkali to tetralin (Table III) gave an "alkali" type

TABLE III

EFFECT OF *n*-VALEROPHENONE (V) AND ALKALI ON THE OXIDATION OF TETRALIN

Additive	r_{max}	t_{max}	t_1	t_3	t_5
0.1 ml. V + 0.1 gm. NaOH	18.8	180	210	670	1325
2.0 ml. V + 0.1 gm. NaOH	15.0	310	230	400	1190
2.0 ml. V + 0.2 gm. NaOH	10.5	230	250	555	1170
As above, oxidized 0.2%	1.6	500	3200	—	—
2.0 ml. V + 0.5 gm. NaOH	8.9	225	350	6000	—

curve but with the maximum rate dependent on the amount of alkali and to a lesser extent on the amount of ketone. The addition of a partially oxidized (0.2%) mixture of 2 ml. of *n*-valerophenone and 0.2 gm. NaOH to tetralin gave a strongly inhibited "alkali" curve (Table III).

A few experiments were also done on the oxidation of tetralin in the presence of *n*-valerophenone and weak acids (Table IV).

TABLE IV

EFFECT OF *n*-VALEROPHENONE (V) AND ACID ON THE OXIDATION OF TETRALIN

Additive	r_{max}	t_{max}	t_1	t_3	t_5	t_{10}	t_{20}
0.5 gm. $C_6H_4(CO_2)_2KH$	12.4	2300	510	900	1190	1775	2840
0.5 gm. $C_6H_4(CO_2)_2KH$ + 0.2 ml. V	11.5	2050	260	575	830	1410	2535
0.5 gm. $C_6H_4(CO_2)_2H_2$	11.2	2450	570	1005	1320	1940	3120
0.5 gm. $C_6H_4(CO_2)_2H_2$ + 0.2 ml. V	11.6	2300	740	1150	1435	2010	3170

The addition of 0.1 ml. of commercial benzaldehyde increased the rate of the "normal" oxidation, but it decreased the rate of the "alkali" reaction. Benzyl alcohol reduced the rate of both "normal" and "alkali" reactions.

The addition, at the beginning of a run, of phenolic compounds such as 2-naphthol, sodium salicylate, γ-2-hydroxyphenylbutyric acid and its sodium salt almost completely inhibited the oxidation of tetralin. Their addition in the middle of a run caused a marked reduction of rate, e.g. 0.1 gm. of γ-2-hydroxyphenylbutyric acid when added to a "normal" run after 1300 sec. caused the rate to drop from 8.8 to 1.1 (cf. 16).

Dehydrating agents such as $CaSO_4$, P_2O_5, and conc. H_2SO_4 completely inhibited the oxidation of tetralin for at least 5000 sec.

Analysis for Products

The infrared spectrum of pure tetralin was compared with the spectra of the products of the "normal" and "alkali" reactions. The "normal" runs showed

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one strong new band at 3470 cm.$^{-1}$ due to O—H stretching in the hydroperoxide. With increasing oxidation hydrogen bonding caused this band to become broader and its maximum to shift to lower wave numbers. There were also some new but weaker bands at lower wave numbers (830, 880, and 912 cm.$^{-1}$) which can also presumably be associated with the hydroperoxide group.

The "alkali" runs showed a number of weak bands and one strong new band at 1683 cm.$^{-1}$ due to C=O stretching. There were no bands due to hydroperoxide, but instead a weak band appeared at 3550 cm.$^{-1}$ which may be due to a naphtholic OH group.

The spectrum of pure 1-tetralone gave a strong band at 1683 cm.$^{-1}$ and a number of weaker bands at lower wave numbers which accounted for most of the differences between the tetralin and "alkali" spectra. For runs lasting less than 6000 sec., i.e. less than about 8% oxidation, the intensity of the 1683 cm.$^{-1}$ band was roughly proportional to the amount of oxidation, but for longer runs its intensity was very much reduced. At 12% oxidation (23,000 sec.) the 1683 band corresponded to only about 2% oxidation, i.e. to about one sixth of the products; since no other new bands appeared the end products of the "alkali" reaction must be rather insoluble in tetralin. Acidification of an "alkali" run eliminated a weak band at 1560 cm.$^{-1}$, but two new bands appeared at 1728 cm.$^{-1}$ and 1715 cm.$^{-1}$. This represents the change from ionized to non-ionized carboxylic acids. The reverse of this process was observed when alkali was added to the products of a "normal" run, i.e. two weak bands at 1728 cm.$^{-1}$ and 1715 cm.$^{-1}$ were replaced by a band at 1560 cm.$^{-1}$. β-2-Carboxyphenylpropionic acid (see below) gave a strong band at 1728 cm.$^{-1}$. The carboxylic acid band at 1715 cm.$^{-1}$ was not characterized.

When alkali was added to the end product of a "normal" run the hydroperoxide was destroyed. Its addition at 6% oxidation gave only 1-tetralone but at 12% a weak new band appeared at 1670 cm.$^{-1}$ which became stronger than the 1683 cm.$^{-1}$ band at 35% oxidation. This band did not appear in the "alkali" reaction. It is probably due to a naphthoquinone.

No other differences of any magnitude were noted in the spectra.

The orange suspension from a 12% oxidized "alkali" run dissolved in water to give a red solution. On acidification the solution turned faint yellow and an acidic, slightly soluble orange oil was obtained. This oil was recrystallized twice from methyl alcohol and identified as 2-hydroxy-1,4-naphthoquinone (m.p. 189° C. (decomp.) (18)).

The green compound was not isolated from an "alkali" run. It was obtained by adding sodium hydroxide to a 12% oxidized "normal" run and heating the mixture at 119° C. for 15 min. The sodium hydroxide pellets turned green; extraction with water followed by acidification gave a dark blue precipitate, m.p. 250° C. (decomp.), identified as 1-(3′,4′-dihydroxy-1′-naphthyl)-3,4-naphthoquinone (m.p. 245° C. (sinters), 255° C. (decomp.) (18)).

A white crystalline compound was obtained from a 7% oxidized "alkali" run by extraction with water and acidification. Recrystallization from boiling water gave β-2-carboxyphenylpropionic acid (m.p. and mixed m.p. 164° C.).

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DISCUSSION

The results given in Fig. 1 and Table I show that the initial catalysis by alkali is soon replaced by a strong inhibition. Although nearly all phenols act as inhibitors in the initial stages of the autoxidation of hydrocarbons, only certain easily oxidized ones such as the naphthols are also effective once the reaction has started (15). The oxidation of tetralin in the presence of strong alkali must therefore produce some powerful inhibitors.

It is clear from the experiments with the solid and liquid phases of a sodium hydroxide run that the inhibitor is only slightly soluble in tetralin, which suggests that the inhibitor is acidic and forms a salt with the alkali.

The very rapid conversion of tetralin hydroperoxide to 1-tetralone by hot alkali (11) was confirmed by infrared analysis. When alkali was added in the middle of a "normal" run the subsequent course of the reaction was of the "alkali" type, but the maximum rate (3.9) was only about one fifth of the rate reached when alkali was added at the start of a run (20.0). This indicates that inhibition depends on the reaction of alkali with 1-tetralone. An "alkali" run has to proceed to just over 1% oxidation before the rate starts to decrease, but when alkali is added in the middle of a "normal" run, the immediate conversion of tetralin hydroperoxide to 1-tetralone almost eliminates the catalytic effect of the alkali. The strong inhibition of the reaction by 1-tetralone and alkali (Table II) is therefore not unexpected; it is probably due in part to a base catalyzed enolization of 1-tetralone to 1-hydroxy-3,4-dihydronaphthalene on the surface of the alkali, and in part to the further oxidation products of 1-tetralone (see below).

The spectrum of colors through which the "alkali" reaction proceeds is very suggestive when compared with the results of Strauss, Bernouilly, and Mautner (18). These workers oxidized 2-hydroxy-1-tetralone in alkaline solution. The solution went through the color changes yellow, brown, greenish-brown, pure green, dirty green, and finally to a permanent orange. They identified the various colored compounds as 1,2-dihydroxynaphthalene (yellow); 3,4;3′,4′-tetrahydroxy-1,1′-dinaphthyl (brown in alkaline solution, pinkish-yellow in acid); 1-(3′,4′-dihydroxy-1′-naphthyl)-3,4-naphthoquinone (dark green in alkali, dark blue in acid); 2-hydroxy-1,4-naphthoquinone (orange in alkali, sodium salt red, yellow in acid). The last named compound was the end product of the reaction and did not further absorb oxygen under their experimental conditions. These substituted naphthols are all acidic and form insoluble salts; they are powerful oxidation inhibitors. While complete reliance can rarely be placed on color reactions alone, the identification in the present work of the last two compounds, and the fact that the "alkali" reaction goes through an almost identical color sequence, would seem to indicate that the first two products are probably also formed.

In agreement with the results of Robertson and Waters (16), no γ-2-hydroxyphenylbutyric acid was detected. These workers found that although this acid was produced by the autoxidation of tetralin and by the decomposition of tetralin hydroperoxide, it was not produced by the autoxidation of 1-tetralone. They concluded that it was formed by an ionic mechanism involving 1-tetra-

lone and tetralin hydroperoxide. In the "alkali" reaction there is of course little or no hydroperoxide present and therefore no γ-2-hydroxyphenylbutyric acid would be expected. Ring scission yields instead β-2-carboxyphenylpropionic acid. The formation of this acid instead of the phenolic acid can be compared with the action of acids and bases on the decomposition of cumene hydroperoxide (12). In the presence of acids this hydroperoxide breaks between the ring and the α carbon atom to yield phenol and acetone, but in the presence of alkali it is the bond between the α and β carbon atoms which breaks to give acetophenone and methane.

No 1-tetralol was detected in the alkaline oxidation of tetralin.

The effect of weak alkali on the oxidation of tetralin was intermediate between "normal" and "alkali" oxidations. This supports the belief that inhibition is due in part to a base catalyzed enolization of 1-tetralone. The amount of enolization, and hence the inhibition, depends both on the strength of the alkali and on its concentration, or more probably on its surface area.

The slight reduction in the rate of oxidation of tetralin by 1-tetralone is in agreement with earlier work (9, 13). Acetophenone behaves in the same way. The greater inhibition produced by partly oxidized 1-tetralone is due to the presence of the inhibitor 3,4-dihydro-1,2-naphthoquinone or its isomer 1-keto-2-hydroxy-1,4-dihydronaphthalene (16). The elimination of the normal induction period by the addition of *n*-valerophenone is similar to the technical use of ketones in promoting the autoxidation of hydrocarbons (19).

The results given in Table III indicate that inhibition by *n*-valerophenone and alkali is probably also due to a base catalyzed enolization on the surface of the alkali. The greater inhibition produced by a partially oxidized *n*-valerophenone and alkali mixture is similar to the increased inhibition produced by oxidized 1-tetralone.

The results in Table IV present some slight evidence that inhibition can also be produced by an acid catalyzed enolization of *n*-valerophenone, although the effect is much less marked than that produced by alkali. The effect shows up most clearly where the catalysis by *n*-valerophenone is compensated for, i.e. in a comparison of the times required to reach a given percentage oxidation for ketone plus potassium hydrogen phthalate and for ketone plus phthalic acid. The latter is a much slower reaction.

Alcohols have been reported both to decrease (15) and to increase (5) the rate of oxidation of tetralin. In the present work benzyl alcohol was found to act as a weak inhibitor.

The complete inhibition brought about by the addition of dehydrating agents at the start of the reaction is probably due to the dehydration of the hydroperoxide directly to 1-tetralone. This prevents chain branching which is normally brought about by scission of the O—O bond of the hydroperoxide.

The very sharp maximum in the "alkali" rate curve could be due to the build-up of sufficient inhibitor to reverse the initial catalyses. However two or more consecutive autocatalytic reactions can lead to periodicity in the reaction rate (14), and a close examination of the rate curves reveals that there are probably at least two subsidiary maxima. The whole course of the "alkali"

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reaction might therefore also be explained as a consecutive series of autocatalytic reactions, the formation of inhibitors accounting for the decrease in height of successive maxima.

CONCLUSION

The usual method of reducing the rate of oxidative deterioration of hydrocarbons is by the addition of certain strong inhibitors such as aromatic amines and naphthols. These inhibitors are, however, gradually oxidized and therefore lose their effectiveness. Inhibition by alkali of the oxidation of tetralin, and presumably of many other hydrocarbons, offers certain advantages in that the concentration of inhibitors is maintained by the oxidation process. The most effective stabilization would probably be obtained by the use of both methods.

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MYRISTIC ACID MONOLAYER AT LOW SURFACE PRESSURES[1]

By G. P. Semeluk,[2] J. W. V. Hahn,[3] and John L. Morrison[4]

ABSTRACT

The surface pressure–area relationships of gaseous myristic acid films at the air–aqueous interface have been measured at very low surface pressures. The acid was spread from petroleum ether solutions. The molecular cohesion was found to be about six times that of gaseous butane under comparable conditions. Some explanation of Moss and Rideal's "double molecule" phenomenon is given.

A number of studies have already been made of myristic acid monolayers on water surfaces (2, 3, 4, 7, 8). Different types of apparatus have yielded concurring results (2, 3, 4) as well as anomalous ones (7, 8). Often insufficient data has been given concerning the methods of spreading, the concentration of the spreading solutions, and the time allowed for evaporation of the solvent, all of which are very important for monolayer studies at the low pressures of gaseous films. It is still correct to say that "Further work on gaseous films, with very sensitive instruments at areas over 1,000 sq. A., is desirable." (1, p. 43).

EXPERIMENTAL

Apparatus

A horizontal film balance of the Langmuir–Adam type (1) was used with an original modification which permitted a sweeping of the whole surface at one time (5). In this modification the head and mica float were vertically moved by a cam. Small stirrups held gold foil ribbons against the bakelized aluminum trough during film measurements. The other ends of the S-shaped ribbons were attached to the mica float to prevent leaks. On raising the head, the small stirrups raised the gold ribbons, and aluminum wire stirrups raised the float. Fragile parts of the head were specially clamped during these operations. The trough had a total area of 960 cm.^{2} and a film dispersing area of 687 cm.^{2}

The forces on the float were measured by phosphor bronze torsion wires. The 5 mil diameter wire measured forces from 0.01 to 1 dyne cm.$^{-1}$. The 3 mil wire measured forces from 0.010 to 0.1 dyne cm.$^{-1}$ to an accuracy of about 0.001 dyne.

Forces were registered by float movements which were transferred through a lever to a mirror pivoted on a torsion wire axle. The balance was used as a null instrument, readings being made on a calibrated dial.

[1]*Manuscript received December 19, 1955.*
Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta. This paper is taken from theses submitted to the University of Alberta in partial fulfillment of the requirements for M.Sc. degrees.
[2]*Graduate student, 1946–48. Holder of a National Research Council Bursary. Present address: Electrochemical Laboratories Corporation, Tulsa, Oklahoma.*
[3]*Graduate student, 1944–46. Present address: Rheumatic Fever Research Institute, Chicago, Illinois.*
[4]*Associate Professor of Chemistry, University of Alberta, Edmonton, Alberta.*

Surface potential measurements were made with a polonium-coated air electrode and a calomel half cell. The potential was amplified by a Dubridge and Brown circuit using an FP 54 electron tube (10). The polonium electrode was mounted on a movable frame to explore the whole surface.

The surface balance was completely enclosed in a double wall copper box which was thermostatted at $20 \pm 0.1°$ C. A small door in a double wall plexiglass front face provided entry to the balance.

Materials

Myristic acid from Eastman Kodak Co. was recrystallized three times from absolute ethanol with norite treatment before each crystallization. The product melted sharply at 58° C.

The spreading solvents were petroleum ether (b.p. 30–35° C.) and benzene (thiophene-free). They were refluxed for 12 hr. over phosphorus pentoxide and then slowly fractionated in a combined reflux and fractionating column.

Solutions of myristic acid in each of the solvents were prepared and used immediately. Concentrations ranged from 0.0011 mgm. myristic acid per ml. to 0.0172 mgm. $ml.^{-1}$ in the case of petroleum ether which was the better solvent.

Procedure

The trough was filled to its brim with 0.01 *N* HCl in conductivity water. The solution had been previously treated with norite to remove surface active impurities. The surface was swept 10 times, the balance head lowered, and the zero point allowed to come to rest.

Each film was spread drop by drop over different parts of the surface from a 0.0878 ml. micropipette. A standard 10 min., determined from a preliminary study of spreading times, was allowed for solvent evaporation and spreading of the film.

Two types of experiments were made. For all areas below 7000 $Å^2$ $molecule^{-1}$, the 5 mil wire was used and the conventional procedure of successively decreasing the surface area was followed. The interval between successive force readings was from 6 to 10 min. For areas above 7000 $Å^2$, the 3 mil wire was used and a single determination of force and area was made. The surface was then swept clean and a new film was spread on a different area. Although the latter method was laborious, each reading taking about 45 min., it avoided any vibrations which cause zero point changes.

Surface potential measurements were determined only on the less dilute films. In very dilute films too few molecules were under the electrode (1 $cm.^2$ in area) to cause a potential change.

Complete details of the great precautions necessary to ensure cleanliness and stability are given elsewhere (9).

RESULTS AND DISCUSSION

The results for myristic acid dispersed from petroleum ether and from benzene are plotted in Fig. 1 as the surface pressure, F dyne $cm.^{-1}$, against the area, A, Angstrom^2 per molecule, following the notation of Adam (1). They are also plotted in Fig. 2 as the product FA against F. In this figure the results

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of Adam and Jessop (2), Guastalla (4), and Allan and Alexander (3) are given for comparison with the present results. The present results, particularly for the single value experiments, are at lower pressures than any reported in the literature.

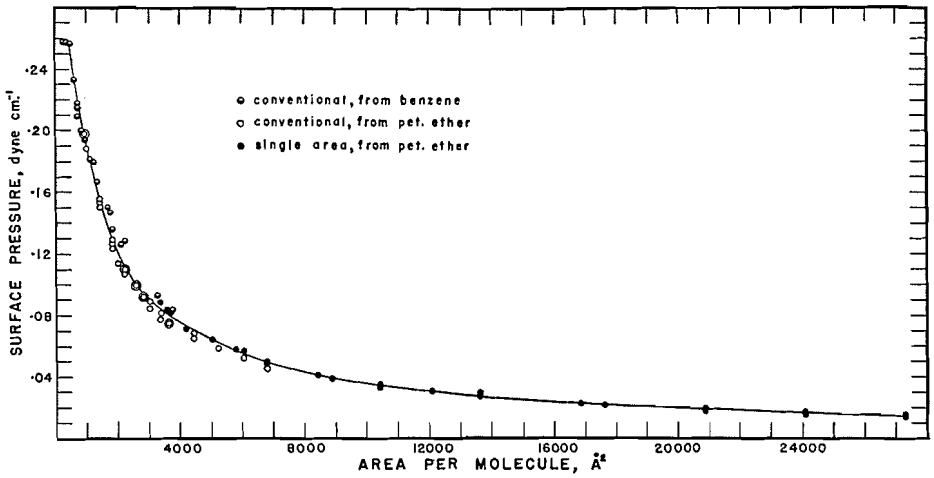

FIG. 1. Surface pressures corresponding to various surface areas occupied by myristic acid molecules on 0.01 *N* HCl aqueous solution.

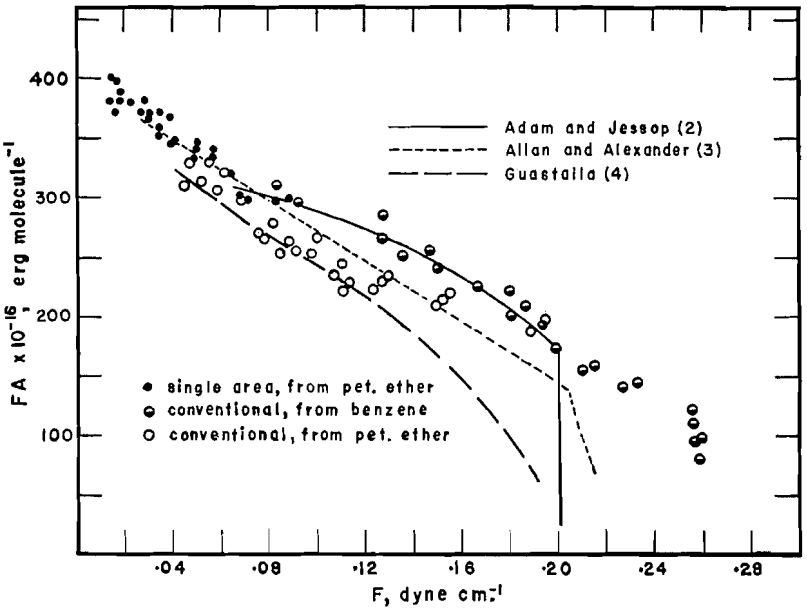

FIG. 2. Comparisons of *FA* versus *F* plots.

Although our results do not agree with those of Moss and Rideal (8), some experimental evidence will be given which may account for their observations. Also, an explanation will be suggested for the observations of Kalousek (7).

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Cohesive Force

Corresponding to van der Waals equation for three dimensions, an equation for two-dimensional surface films (1, p. 120) would be

$$[1] \qquad (F+\alpha/A^2)(A-\beta) = kT$$

where F and A are the same as above, α/A^2 is the cohesive force, β is the "excluded area" of the molecules, k is Boltzmann's constant, and T the absolute temperature. In the present case, at very low surface pressures (<0.1 dyne cm.$^{-1}$), β becomes negligible compared with A and the equation reduces to

$$[2] \qquad FA = kT-\alpha/A.$$

This equation was applied to the single point determinations (29 in number) made on the 3 mil wire. By plotting FA against $1/A$ and using the method of least squares to obtain the straight line, we obtained the equation

$$FA = 402-4.02\times10^5/A.$$

The theoretical value of kT at 293° K. is 404 ergs per molecule when the area is expressed in Å^2.

Arbitrarily choosing an area of 12,000 Å^2 per molecule, we calculate the cohesive force α/A^2 to be 2.80×10^{-3} dyne cm.$^{-1}$ molecule^{-1}. If the film thickness is assumed to be 4.5 Å (1, p. 45), then α/A^2 is equivalent to 6.1×10^{-2} atm. cm.$^{-2}$ in three dimensions.

This cohesive force may be compared with that of butane under similar conditions. Thus, at $A = 12{,}000$ Å^2 per myristic acid molecule, F is equal to 0.03 dyne cm.$^{-1}$. The equivalent pressure in three dimensions at 20° C. is 0.66 atm. (1, p. 45). Under the same conditions, and for ideal behavior, the molar volume of butane is 36.4 liters. The van der Waals constant for butane, a, is 14.5 liter^2 atm. Thus, the cohesive forces are $a/V^2 = 1.1\times10^{-2}$ atm. for butane and $\alpha/V^2 = 6.1\times10^{-2}$ atm. for myristic acid. This is a very reasonable value for myristic acid in the gaseous film state.

Equation [2] was applied to the results of the conventional force–area experiments, which cover a somewhat higher pressure range than the single experiments. Low values for FA at zero pressure were obtained. For example, for benzene solutions FA was equal to 335. This is not surprising as the range of pressure is from 0.08 to 0.22 dyne, the latter being quite close to the "vapor pressure" of the "liquid" myristic acid film.

However, when extrapolations were made on FA versus F straight lines, the least square values at zero surface pressure were 410, 405, and 419 respectively for single runs, and for conventional runs from petroleum ether and from benzene. There is no theoretical justification for this type of *linear* extrapolation. At the same time, it is apparent that measurements must be made well below the "vapor pressure" of the "liquid" film in order that the van der Waals type of extrapolation be valid.

Latent Heat of Vaporization

Adam and Jessop (2), using the Clapeyron equation, have calculated the latent heat of vaporization of myristic acid liquid monolayer to be 3200 cal.

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mole^{-1} at 14.5° C. The latent heat can also be estimated by combining their vapor pressure measurements at 14.5° (0.203 dyne) with ours at 20° (0.258 dyne from Fig. 2) in the Clausius–Clapeyron equation. By making the approximation that the latent heat is constant over this temperature range, we obtain the value of 730 cal. mole^{-1}. Two comments may be made concerning this value: (1) one would expect the latent heat to fall off rapidly with temperature near the "critical temperature" of the gaseous film (est. 30–35° (2)); (2) the present calculation takes more account of the effect of the substrate than does the method using the areas of the liquid and gaseous films at the terminal points of the liquid–gas equilibrium line.

The Island Phenomenon

For areas less than 6000 Å^2 per molecule, force readings taken at successively smaller areas, in each case 10 min. after spreading, exhibited an erratic behavior. A typical experiment is given in Table I. The surface potential apparatus showed that the film was not homogeneous. Wherever a drop of spreading

TABLE I

Area, Å^2 molecule^{-1}	Force, dyne cm.$^{-1}$	*FA*
Experiment No. 73 (0.0878 ml. of 0.0043 mgm. ml.$^{-1}$ in petroleum ether):		
6820	0.045	307
6020	0.097	583
5220	0.09	470
4410	0.09	395
3610	0.126	455
2810	0.12	335
2010	0.172	346
Repeat of Experiment No. 73 after decompression:		
6820	0.045	307
6020	0.052	313
5220	0.058	303
4410	0.068	300
3610	0.074	267
2810	0.091	256
2010	0.113	227

solution had been placed, the potential was 5 to 10 mv. more positive. Other parts of the surface showed no change from the potential of a clean surface. These observations suggest the presence of islands of unspread myristic acid. Since the islands did not disperse in a convenient length of time, a procedure was devised to disperse them. The film was compressed to one-seventh of its original area to merge the islands, then it was expanded very slowly (10–15 min.). Surface potentials varied over the surface to a smaller extent (2–6 mv.) and no clean surface potentials were found. After complete decompression, the compression was repeated with much more consistent results. It was found that the increased time did not accumulate much contamination.

The island phenomenon was observed for both benzene and petroleum ether solvents. It was also found to depend on the concentration of the dis-

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persing solution. For example, when measurements were made at the lowest pressure range with the 3 mil torsion wire, solutions more dilute than 0.0043 mgm. per ml. spread completely in 10 min.

Further observations help to account for the island phenomenon. Immediately after placing the dispersing solution on the surface, the pressure increased momentarily to a fairly high value (approx. 0.3 dyne), then rapidly decreased practically to zero within a minute, and finally increased slowly for the next few minutes. Each drop of solution formed a lens of from 2 to 3 cm. diam. According to Harkins' theory of spreading (6), there is a monomolecular layer of hydrocarbon in equilibrium with a visible liquid lens. This would account for the high initial pressure. Apparently this monomolecular layer (5–10 Å thick) is not able to drag many myristic acid molecules with it. Most of them remain at the site of the lens, and the lens decreases largely by spreading as a monolayer and *then* evaporating.

The erratic force measurements can be explained[5] by the suggestion that each island of myristic acid will exert a dynamic vapor pressure in excess of the final static pressure of the homogeneous film. The mica float would pick up these dynamic pressures when islands floated near to it. Conversely, the absence of islands near the float would be similar to a two-dimensional vacuum. It is to be noted that this phenomenon is not the same as the incomplete spreading caused by contamination. In the latter case, the surface pressure is uniform over the whole surface.

Double Molecules

Moss and Rideal (8) determined the force–area relations of myristic acid films within the molecular area range of 1000 to 15,000 Å^2. They found a nearly constant value for FA of about 200 over the whole gaseous range. They concluded that the film consists of extremely stable double molecules, and that these follow the two-dimensional ideal gas law.

Moss and Rideal's spreading method differed from the one used here. Instead of obtaining successively smaller areas by moving a barrier towards the float, they used a fixed area. They spread a film from one drop of a solution, then they made a force measurement. Another drop was placed on top of the existing film to obtain a smaller molecular area and again a force measurement was taken. A series of such measurements on films spread one on top of the other comprised their experiment.

We duplicated the results of Moss and Rideal to a large extent by repeating their method of spreading on a fixed area. Initially 0.0878 ml. of a petroleum ether solution containing 0.0021 mgm. myristic acid per ml. solution was placed on a surface area of 662 sq. cm. After complete spreading of the film, duplicate amounts were placed successively on top of each film. The results are given in Fig. 3. In view of the fact that the first film spread on a clean surface did not give a FA value near 200 and the further fact that the island phenomenon disappeared as the initial areas became much greater than

[5]*The first referee has observed even* negative *pressures under conditions similar to the above and suggests that the observations may be accounted for by a cooling caused by the evaporating volatile solvent.*

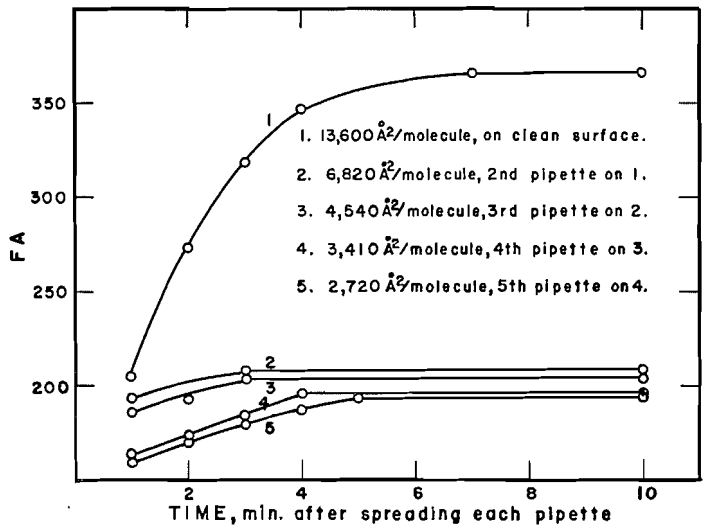

FIG. 3. The changes of surface pressure with time after adding one spreading solution on top of another at constant surface area.

7000 Å² per molecule, it is possible that a critical concentration of the spreading solution exists above which there is spontaneous double molecule formation.[6,7]

As the island phenomenon was most pronounced with solutions of concentration 0.0043 mgm. ml.$^{-1}$ and greater, it is believed that this is near the critical concentration. Unfortunately, Moss and Rideal, in common with most workers in this field, did not report their spreading solution concentrations. Moreover their experimental temperature (17°) would be more favorable to double molecule formation than ours.

The time of spreading is very important. In our case, the one minute reading for each pipette (Fig. 3) is obtained *after* the rise caused by the petroleum ether has fallen off. Adam (1, p. 31) suggests taking readings within one minute. Moss and Rideal allowed "a few minutes" between readings. It is apparent from our results that even for such a volatile solvent as petroleum ether (b.p. 30–35°) at least six minutes are required to obtain a steady force reading.

It may be possible to explain Kalousek's anomalous results for myristic acid (7). His results for the ester ethyl hexadecanedicarboxylate are normal, extrapolating to an *FA* value of about 400. However, his myristic acid *FA* values only reach about 65 at 0.014 dyne cm.$^{-1}$. Although he gives no data on the concentrations of his spreading solutions, a clue to their magnitude may be given in his statement—"This condition is fulfilled with light petroleum (b.p. 70°) which in amounts of 1 mm.^{3}/100 cm.^{2} evaporates in about 1 minute." If he used this volume for his spreading solutions, then his concentrations would be of the order of 10 times the present ones. Such high concentrations

[6]*The significance of the concentration of the spreading solution was not fully realized at the time these measurements were made so that other initial spreading concentrations were not tested.*

[7]*The first referee has suggested that Moss and Rideal* may *have used water as a substrate* and *an uncoated metal trough for their balance. Either or both these differences in method may account for their anomalous results.*

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would be very conducive to the occurrence of islands and double molecules. In his efforts to overcome the effect of residual solvent on the surface pressure, Kalousek may have become involved in a more serious error in the spreading of myristic acid films.

Solvents

Each of the solvents, benzene and petroleum ether, has its disadvantages. Our low boiling petroleum ether evaporated too quickly, which was conducive to island formation. Benzene leaves a significant residual pressure and increases the rate of contamination of the surface.

Because of residual pressure, measurements made on benzene solutions at areas greater than 2750 $Å^2$ were not reliable. At surface pressures greater than 0.2 dyne, where the residual pressure was less than one-tenth of the total pressure, the benzene and petroleum ether results coincided. The surface vapor pressure of myristic acid was the same from both solvents.

The change in surface potential for the residual benzene, compared with the clean surface, was about −3 mv. at 10 min. Myristic acid changes the potential in the opposite direction. Petroleum ether evaporated completely in 10 min. to leave the surface potential unchanged. Thus, the latter is the more suitable solvent for surface potential measurements.

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APPLICATION OF THE VIBRATIONAL SUM RULE TO HALOGENATED ETHYLENES[1]

By H. J. Bernstein

ABSTRACT

The vibrational sum rule has been applied to the fluoro-chloro-bromo-ethylenes and good agreement obtained between observed frequency sums and those calculated on the basis of additivity considerations. Two unobserved frequencies for *trans* dibromoethylene have been calculated and the in-plane and out-of-plane sums for some molecules not yet investigated. Several ambiguities with regard to some halogenated ethylenes have been resolved and several assignments which merit reinvestigation have been indicated.

Considering the zero-point energy in a homologous series of molecules to be an additive property, analogous to the heat of atomization for example, indicated that the sum of the frequencies of the fundamental modes of vibration could be treated as an additive property (2). The additivity scheme describing these properties was one in which contributions from bonds, interactions between neighboring bonds and/or atoms, and interactions between next neighboring bonds, etc., were taken into account (1).

New vibrational data for several halogenated ethylenes have been reported recently and it seems worth while at this time to show the kind of agreement that can be obtained between observed frequency sums and those calculated on the basis of the additivity model. On the strength of this agreement it is then possible to predict some frequency sums for molecules which as yet have not been investigated spectroscopically and also disclose existing assignments which merit reinvestigation.

The relations derived (1) for the substituted ethylenes $C_2X_{4-n}Y_n$ are given in Table I. In making use of the sum rule* it is often required to estimate two

TABLE I

$\sum\nu$

n		P	a	b	c	d
0	C_2X_4	1				
1	C_2X_3Y	1	1			
2	*cis* $C_2X_2Y_2$	1	1			1
2	*trans* $C_2X_2Y_2$	1	1		1	
2	*asym* $C_2X_2Y_2$	1	1	1		
3	C_2XY_3	1	0	1	1	1
4	C_2Y_4	1	−2	2	2	2

unobserved missing sums when the parameters of Table I have been evaluated from the five minimum data. To illustrate the agreement obtained under these

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**The sums formed from the observed fundamental frequencies include gas and/or liquid and/or dilute solution values for the frequencies since vapor state data are not always available.*

conditions, five of the six observed sums for the bromoethylenes have been used to evaluate four sets of values for the parameters of Table I and then used to calculate the unobserved frequency sum for the *trans* molecule and the sixth observed sum. The results are shown in Table II in which the dashes

TABLE II
$\sum\nu$

	Observed	Calculated			
C_2H_4	21597[a]	21648	—	—	—
C_2H_3Br	17795[b]	—	17770	—	—
cis $C_2H_2Br_2$	13920[c]	—	—	—	—
trans $C_2H_2Br_2$	—	13727	13710	13813	13788
asym $C_2H_2Br_2$	13810[d]	—	—	—	—
C_2HBr_3	9730[c]	—	—	9755	—
C_2Br_4	5518[e]	—	—	—	5467

[a] *Arnett, R. H. and Crawford, B. L. J. Chem. Phys. 18: 118. 1950; with the new value of* $\nu_5(b_{1g})$ *found by B. P. Stoicheff, J. Chem. Phys. 21: 755. 1953.*
[b] *Charette, J. and de Hemptinne, M. Bull. classe sci., Acad. roy. Belg. 38: 934. 1952.*
[c] *Reference (3).*
[d] *de Hemptinne, M. Trans. Faraday Soc. 42: 7. 1946.*
[e] *Reference (7).*

represent frequency sums used to evaluate the parameters. Comparison of the observed and calculated value for the sixth sum indicates agreement to within ± 50 cm.$^{-1}$. The average of the calculated values of the unobserved *trans* sum has an average deviation from the mean of 41 cm.$^{-1}$.

Since the potential energy function for the nine in-plane and three out-of-plane vibrations of a substituted ethylene may be separated, one might expect that the relations of Table I are valid both for the in-plane and for the out-of-plane frequency sums as well as for the total sums. This has already been verified for the chloroethylenes (2).

In Tables III and IV the calculated frequency sums for the in-plane and out-of-plane modes for the bromoethylenes are given, corresponding to the calculations shown in Table II for the total sums.

TABLE III
IN-PLANE SUMS FOR BROMOETHYLENES

	Observed	Calculated			
C_2H_4	18678[a]	18682	—	—	—
C_2H_3Br	15364[b]	—	15362	—	—
cis $C_2H_2Br_2$	12020[c]	—	—	—	—
trans $C_2H_2Br_2$		11943	11951	11959	11957
asym $C_2H_2Br_2$	11831[d]	—	—	—	—
C_2HBr_3	8394[c]	—	—	8396	—
C_2Br_4	4742[e]	—	—	—	4736

All footnotes are the same as for Table II.

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TABLE IV

OUT-OF-PLANE SUMS FOR THE BROMOETHYLENES

	Observed	Calculated			
C_2H_4	2919[a]	2966	—	—	—
C_2H_3Br	2431[b]	—	2408	—	—
cis $C_2H_2Br_2$	1900[c]	—	—	—	—
trans $C_2H_2Br_2$		1785	1762	1854	1831
asym $C_2H_2Br_2$	1979[d]	—	—	—	—
C_2HBr_3	1336[e]	—	—	1359	—
C_2Br_4	775[e]	—	—	—	729

All footnotes are the same as for Table II.

From Table III it is seen that the calculated sum for *trans* $C_2H_2Br_2$ is very nearly the same for all solutions and that the agreement for the sixth sum is quite good. Since all but one of the in-plane fundamentals are known (3) for *trans* $C_2H_2Br_2$ the unobserved fundamental may be estimated from the sum in Table III to be 149 ± 6 cm.$^{-1}$. Similarly the unobserved out-of-plane mode (3) for *trans* $C_2H_2Br_2$ may be estimated at 170 ± 50 cm.$^{-1}$. Applying the above method to the recent data (7) for the fluorochloroethylenes gives the results shown in Tables V and VI.

TABLE V

IN-PLANE SUMS FOR THE FLUOROCHLOROETHYLENES

	Observed[a]	Calculated			
C_2F_4	8234	8193	—	—	—
C_2F_3Cl	7591	—	7612	—	—
cis $C_2F_2Cl_2$		6985	7004	6904	6944
trans $C_2F_2Cl_2$	6909	—	—	—	—
asym $C_2F_2Cl_2$	7066	—	—	—	—
C_2FCl_3	6380	—	—	6360	—
C_2Cl_4	5771	—	—	—	5812

[a]*The data are from Reference (7).*

TABLE VI

OUT-OF-PLANE SUMS FOR THE FLUOROCHLOROETHYLENES

	Observed[a]	Calculated			
C_2F_4	1104	1102	—	—	—
C_2F_3Cl	1073	—	1071	—	—
cis $C_2F_2Cl_2$		1054	1055	1051	1052
trans $C_2F_2Cl_2$	998[b]	—	—	—	—
asym $C_2F_2Cl_2$	1044	—	—	—	—
C_2FCl_3	979	—	—	978	—
C_2Cl_4	914	—	—	—	916

[a]*The data are from Reference (7).*

[b]*This sum includes one frequency calculated by means of a normal coordinate treatment which gives over-all agreement between observed and calculated frequency of 1 to 2% for all the members of the series* $C_2F_4 \rightarrow C_2Cl_4$ *(Reference (7)).*

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It is evident from Table I that the average of the frequency sums for *cis*, *trans*, and *asym* disubstituted ethylenes lies on a parabola passing through the sums for the other molecules when the frequency sum is plotted against the number of substituents n. Thus the X, Y, Z substituted ethylenes may be treated as the X, X, Z substituted methanes and the relations between their sums expressed in terms of the six parameters of Table III in Reference (1) and shown again for convenience in Tables VII and VIII. In Table VII the sums calculated with the least squares values of the parameters are compared with the observed sums for the chloro- and fluoro-ethylenes. In all cases the value for the disubstituted molecule is asterisked and is the average of the sums for the isomeric disubstituted molecules. The agreement between observed and calculated sums is rather good, being within ± 25 cm.$^{-1}$ for the in-plane modes and ± 10 cm.$^{-1}$ for the out-of-plane. The asterisked sum is only roughly

TABLE VII

	Parametric relations						$\sum\nu_{\text{in-plane modes}}$			$\sum\nu_{\text{out-of-plane modes}}$		
Molecule	P	α	β	γ	Δ_1	Δ_2	Calc.†	Obs.	Obs. − calc.	Calc.‡	Obs.	Obs. − calc.
C_2H_4	1						18697	18678[a]	−19	2919	2919[a]	0
C_2H_3Cl	1	1					15623	15659[b]	34	2453	2459[b]	+ 6
$C_2H_2Cl_2$*	1	2			−1		12442	12431[b]	−11	1962	1959[b]	− 3
C_2HCl_3	1	3			−3		9156	9133[b]	−23	1449	1447[b]	− 2
C_2Cl_4	1	4			−6		5763	5771[c]	8	913	914[c]	+ 1
C_2H_3F	1		1				16246	16251[d]	5	2514		
C_2HF_3	1		3			−3	11010	11004[e]	−6	1607	1610[e]	+ 3
C_2F_4	1		4			−6	8226	8234[c]	18	1105	1104[c]	− 1
C_2Cl_3F	1		1	3	−3		6370	6380[c]	10	977	979[c]	+ 2
C_2ClF_3	1	−2	3	3		−3	7601	7591[c,f]	−10	1074	1072[c,f]	− 2
$C_2Cl_2F_2$*	1	−2	2	4	−1	−1	6982	7004[c]	+22	1031	1020[c]	−11
$C_2H_2F_2$*	1		2			−1	13683	13463[g]		2076	2127[h] 2004[i]	
C_2H_2FCl*	1		1	1			13060			2025		
C_2Cl_2HF*	1		1	2	−1		9768			1513		
C_2F_2HCl*	1	−1	2	2		−1	10386	10422[j]		1565	1568[j]	

**For these molecules the sum is* $\frac{1}{3}(\sum\nu_{cis}+\sum\nu_{trans}+\sum\nu_{asym})$.

†The least squares values for the parameters used to obtain these calculated sums are $P = 18697$, $\alpha = -3074.2$, $\beta = -2451.2$, $\gamma = -3185.8$, $\Delta_1 = 106.1$, *and* $\Delta_2 = 111.0$, *all in cm.*$^{-1}$.

‡The least squares values for the parameters used to obtain these calculated sums are $P = 2919$, $\alpha = -467$, $\beta = -406$, $\gamma = -489$, $\Delta_1 = 23.2$, *and* $\Delta_2 = 31.9$, *all in cm.*$^{-1}$.

[a] *Same as for Table II.*

[b] *Reference (2), except data for* C_2HCl_3 *are taken from Allen, G. and Bernstein, H. J. Can. J. Chem. 32: 1044. 1954.*

[c] *Reference (7).*

[d] *Torkington, P. and Thompson, H. W. Trans. Faraday Soc. 41: 236. 1945.*

[e] *Mann, D. E., Acquista, N., and Plyler, E. K. J. Chem. Phys. 22: 1586. 1954.*

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[g] *Sum for* $CH_2{=}CF_2$ *only. Smith, D. C., Nielsen, J. R., and Classen, H. H. J. Chem. Phys. 18: 326. 1950; Edgell, W. F. and Byrd, W. E. J. Chem. Phys. 17: 740. 1949; Torkington, P. and Thompson, H. W. Trans. Faraday Soc. 41: 236. 1945; and Edgell, W. F. and Altel, C. J. J. Chem. Phys. 22: 1983. 1954.*

[h] *Sum for* $CH_2{=}CF_2$ *only from Edgell et al. (Ref. g) and Torkington and Thompson (Ref. g).*

[i] *Sum for* $CH_2{=}CF_2$ *only from Smith et al. (Ref. g).*

[j] *Data for* $CF_2{=}CHCl$ *only from Nielsen, J. R., Liang, C. Y., and Smith, D. C. J. Chem. Phys. 20: 1090. 1952. These are included to indicate that the assignment of the above authors is consistent with the sum rule.*

TABLE VIII

Molecule	Parametric relations						$\sum\nu_{\text{in-plane modes}}$		$\sum\nu_{\text{out-of-plane modes}}$		
	P	α	β	γ	Δ_1	Δ_2	Calc.†	Obs.	Calc.‡	Obs.	
C_2H_4	1						18697	18678[a]	2919	2919[a]	
C_2H_3Br	1	1					15365	15362[b]	2440	2431[b]	
C_2HBr_3	1	3			−3		8387	8394[c]	1320	1336[c]	
C_2H_3F	1		1				16246	16251[d]	2514		
C_2HF_3	1		3			−3	11010	11004[e]	1607	1610[e]	
C_2F_4	1		4			−6	8226	8234[f]	1105	1104[f]	
C_2BrF_3	1	−2	3	3		−3	7354	7353[g]	1043	1043[g]	
$C_2H_2Br_2$*	1	2			−1		11929	11925[h]	1907	1935[h]	
C_2Br_4	1	4			−6		4743	4742[f]	679	674[f]	
$C_2H_2F_2$*	1		2			−1	13683	13463[i]	2076	2127[j]	2004[k]
C_2Br_3F	1		1	3	−3		5613		830		
$C_2Br_2F_2$*	1	−2	2	4	−1	−1	6484		951		
C_2H_2FBr*	1		1	1			12806		2006		
C_2Br_2HF*	1		1	2	−1		9261		1445		
C_2F_2HBr*	1	−1	2	2		−1	10136		1540		

*For these molecules the frequency sum is $\frac{1}{3}[\sum\nu_{cis}+\sum\nu_{trans}+\sum\nu_{asym}]$.

†*Values of P, β, and Δ_2 are the same as for Table VII (footnote †), and $\alpha = -3332$, $\Delta_1 = 104.5$ were evaluated from the observed sums for C_2H_3Br, C_2HBr_3, and C_2Br_4 averaging the solutions for the three pairs of equations. $\gamma = -3440$ was then found from the observed sum for C_2BrF_3.*

‡*Values of P, β, and Δ_2 are the same as for Table VII (footnote ‡), and $\alpha = -479$, $\Delta_1 = 54$ were evaluated from the observed sums for C_2H_3Br, C_2HBr_3, and C_2Br_4 by averaging the solutions for the three pairs of equations. $\gamma = -507$ was then found from the observed sum for C_2BrF_3.*

[a,b,c,d,e]*Same as for Table II.*

[f]*Reference (7).*

[g]*Mann, D. E., Acquista, N., and Plyler, E. K. J. Chem. Phys. 22: 1199. 1954.*

[h]*Average of the cis and asym only from Reference (3) and M. de Hemptinne, Trans. Faraday Soc. 42: 7. 1946, respectively.*

[i]*Same as g of Table VII.*

[j]*Same as h of Table VII.*

[k]*Same as i of Table VII.*

equal to the sum for each isomer so that observed sums for CF_2=CHCl are given for comparison to indicate only that no gross error in assignment has been made. This is the case also for $C_2H_2Br_2$ and $C_2H_2F_2$ given in Table VIII. In Table VIII the least squares values of the parameters were not obtained since there is only one equation for evaluating γ. However, the same values of P, β, and Δ_2 were used as for the molecules in Table VII and α and Δ_1 obtained from the observed sums for C_2HBr_3, C_2H_3Br, and C_2Br_4 by averaging the solutions from the three pairs of equations thus provided. The value for γ was then obtained from the observed sums for C_2F_3Br. The estimated error in the calculated sums for the bromofluoroethylenes is about ± 50 cm.$^{-1}$ for the in-plane sums and about ± 25 cm.$^{-1}$ for the out-of-plane sums.

Several ambiguities with regard to the assignments of some halogenated ethylenes can be resolved by comparison of the observed and calculated sums. Also several assignments which require reinvestigation are indicated. In C_2H_3Br the assignment (Ref. *b* in Table VII) for the out-of-plane modes is consistent with the sum rule whereas that given by Kohlrausch (4) and that given in Ref. *d* of Table VII are not. In C_2H_3F the assignment given in Ref. *d* of Table VII for the out-of-plane modes is not consistent with the sum rule. For C_2F_3Cl the assignment of Mann *et al.* (5) for the in-plane modes is con-

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sistent with the sum rule. For C_2F_3Cl the assignment of Mann *et al.* (5) for the in-plane modes is consistent with the sum rule but that of Smith *et al.* (Ref. *f* of Table VII) is not. For C_2FCl_3 the assignments of Mann and Plyler (6) and Nielsen *et al.* (Ref. *f* of Table VII) for the in-plane modes are not consistent with the sum rule. All recent assignments for the fluorochloroethylenes of Mann and Plyler (7) are consistent with the sum rule.

As shown in Ref. (2) the theory predicts the following relationship between the frequency sum of the molecules and their deuterated analogues:

$$\sum\nu_{C_2H_{4-n}X_n} - \sum\nu_{C_2D_{4-n}X_n} = (1-n/4)\left\{\sum\nu_{C_2H_4} - \sum\nu_{C_2D_4}\right\}.$$

This equation is valid also for each of the isomeric disubstituted ethylenes. Using this equation for the in-plane and out-of-plane sums, the sums shown in Table IX have been calculated for some deuterated fluoro- and bromo-

TABLE IX

	$\sum\nu_{\text{in-plane}}$		$\sum\nu_{\text{out-of-plane}}$	
	Calc.	Obs.	Calc.	Obs.
C_2D_3Br	12044		1912	
cis $C_2D_2Br_2$	9814	9767[a]	1554	1545[a]
1.1 $C_2D_2Br_2$	9625		1663	
C_2DBr_3	7291		1163	
C_2D_3F	12933		2003	
1.1 $C_2D_2F_2$	11257	11259[b]	1730	1755[b]
C_2DF_3	9901	9803[c]	1437	1431[c]

[a] *Professor M. de Hemptinne, private communication, Oct. 21, 1954.*
[b] *From the data of Edgell and Altel (Ref. g of Table VII).*
[c] *Ref. e, Table VII.*

ethylenes. The sums for C_2D_4 are given in Ref. *a* of Table II. The corresponding calculations for the frequency sum of the deuterated chloroethylenes have been given elsewhere (2).

Graphical Methods

If the frequency sums for two homologous series of substituted ethylenes are quadratic functions of the number of substituents, then there is a quadratic relationship between the frequency sums for the molecules of one series and those of the corresponding molecules of the other series (3). It has been discussed previously (3) under what conditions this relationship between the two sets of frequency sums becomes nearly linear, namely, if the ranges of frequency sums for both series are large and of the same order of magnitude and/or the deviation from linearity of the frequency sum as a function of the number of substituents is small. These conditions are fulfilled approximately for the chloro-, fluoro-, and bromo-ethylenes and the linear plots for the in-plane sums are shown in Fig. 1. To form the average of the sums of the isomeric disubstituted molecules the calculated sum for the molecule whose spectrum is unknown has been used (see Tables II to VIII). In Fig. 2 the corresponding

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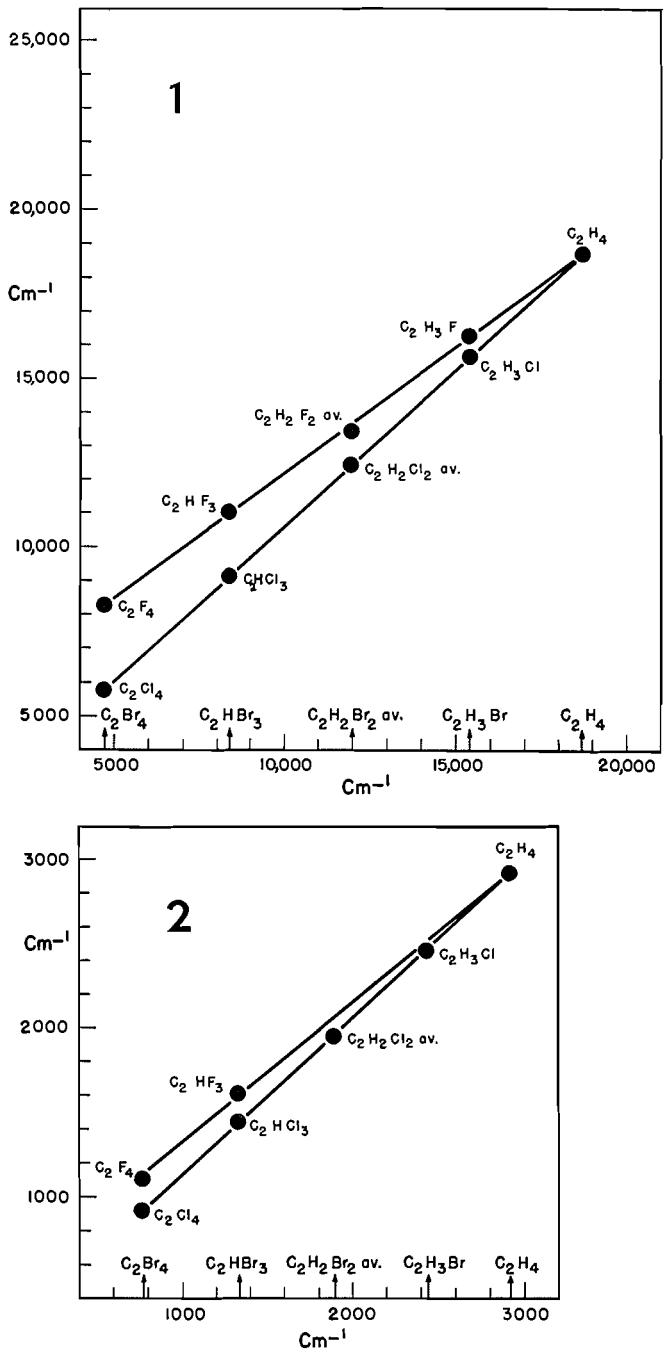

FIG. 1. The in-plane sums for the fluoro- and chloro-ethylenes plotted against the in-plane sums for corresponding bromoethylenes.

FIG. 2. The out-of-plane sums for the fluoro- and chloro-ethylenes plotted against the out-of-plane sums for the corresponding bromoethylenes.

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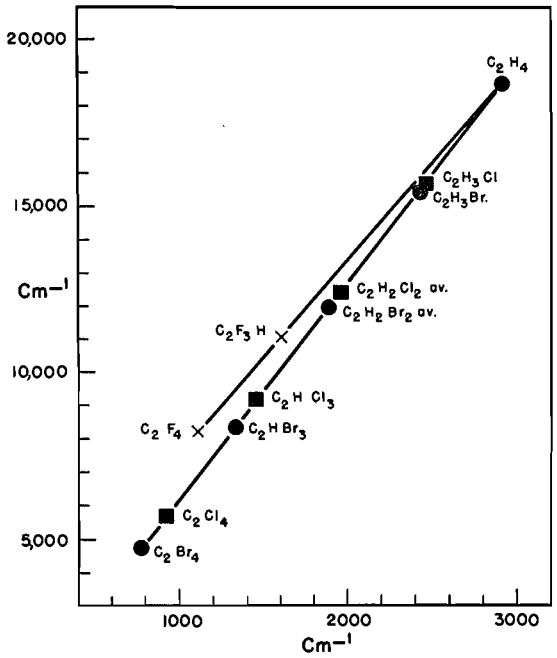

FIG. 3. The in-plane vs. out-of-plane sums for the fluoro-, chloro-, and bromo-ethylenes.

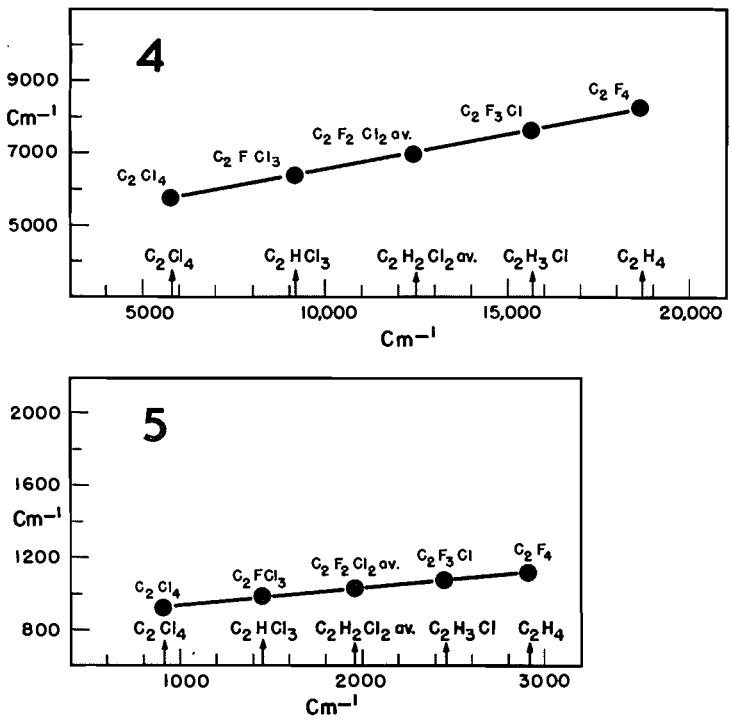

FIG. 4. The in-plane sums for the fluorochloroethylenes vs. the in-plane sums for the chloroethylenes.

FIG. 5. The out-of-plane sums for the fluorochloroethylenes vs. the out-of-plane sums for the chloroethylenes.

plots are given for the out-of-plane sums. It is apparent that a good internal check in the assignments for such a series is to plot the frequency sum for the in-plane modes against that for the out-of-plane modes. The resulting straight lines for the chloro-, bromo-, and fluoro-ethylenes are shown in Fig. 3. It is fortuitous that the points for the chloro- and bromo-ethylenes lie on the same straight line in Fig. 3. In Fig. 4 the in-plane sums for the fluorochloroethylenes are plotted against those for the chloroethylenes on the same scale and Fig. 5 shows the corresponding plot for the out-of-plane sums. The chlorofluoroethylenes and chlorobromoethylenes also fulfill approximately the conditions for obtaining linear plots so that the frequency sums for the chlorobromoethylenes may be estimated from the straight line given by the end members of the two series and reading off these sums from the values for the corresponding chlorofluoroethylenes. These estimates are given in Table X.

TABLE X

	$\sum \nu_{\text{in-plane}}$	$\sum \nu_{\text{out-of-plane}}$
C_2ClBr_3	5015	713
$C_2Cl_2Br_2$	5260*	780*
C_2Cl_3Br	5520	830

**Asterisk has same significance as for Table VII.*

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A SYSTEM OF MOLECULAR THERMOCHEMISTRY FOR ORGANIC GASES AND LIQUIDS[1]

By Keith J. Laidler

ABSTRACT

An analysis has been made of the heats of formation and combustion of organic gases and liquids, and of the heats of vaporization of liquids. The work has been done as far as possible with homologous series, in order to discover systematic effects. The data are converted into heats of atomization, i.e., the heats required to convert the gases or liquids into their constituent atoms. It is shown that the heats of atomization of the gaseous aliphatic hydrocarbons (paraffins, olefins, and acetylenes) can be accurately represented by a scheme in which a distinction is made between primary, secondary, and tertiary carbon–hydrogen bonds, and between bonds that are next to, and next but one to, multiple bonds. For aromatic molecules an appropriate correction for resonance is proposed. For other types of compound it is found that suitable values for the various bonds (e.g., C–CHO, C–OH) will give rise to good agreement with experiment.

It is shown that to a reliable approximation heats of vaporization are also amenable to the same treatment. Since this is so it is possible to assign bond values on the basis of which it is possible to make predictions about heats of formation of liquids.

A system of coefficients is worked out by means of which the numbers of atoms of various kinds in a molecule can be expressed in terms of the numbers of the different kinds of bonds. On the basis of these it is shown how bond contributions to heats of formation and heats of combustion can be calculated. A table (Table X) gives the contributions proposed for the heats of atomization, heats of formation, and heats of combustion for both gases and liquids.

INTRODUCTION

Various attempts have been made from time to time to devise systems that will enable reliable values of heats of formation and of heats of combustion to be deduced on the basis of chemical structure. Very approximate values can be calculated assuming strict bond additivity, using bond strengths such as those listed by Pauling (26) and by Syrkin (37); however such a procedure can lead to considerable errors in organic molecules of even only moderate complexity. Various schemes for the inclusion of terms for interactions (27) between bonds or between atoms have been proposed, notably those of Taylor, Pignocco, and Rossini (42), Tatevskii (38, 39, 40), and Bernstein (4). Of these workers Taylor, Pignocco, and Rossini did not specifically consider heats of formation, but Tatevskii showed that reliable predictions could be made for paraffins by recognizing three different types of carbon–hydrogen bonds and 10 different types of carbon–carbon bonds. Bernstein later showed that equally good agreement could be obtained with fewer types. In the present paper it is shown that satisfactory agreement for the lower paraffins is obtained by treating all carbon–carbon bonds as the same and recognizing three different types of carbon–hydrogen bonds. For olefins and acetylenes six additional types of bonds are required, and in most cases it is shown that the scheme is equivalent to, but much simpler than, a scheme of near-neighbor interactions.

The present paper is restricted to organic compounds containing carbon, hydrogen, oxygen, and nitrogen only, but the methods are readily extended to

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other substances. Bond contributions are arrived at that will allow heats of atomization, formation, and combustion of gaseous and liquid substances to be estimated in a reasonably reliable manner. The procedures employed are necessarily empirical ones, but as far as possible an attempt has been made to provide some theoretical basis for the method; this has been done by taking the heats of atomization as the fundamental quantities to be analyzed. The method differs in this respect from certain others, such as the very useful one of Andersen, Beyes, and Watson (3, 19) in which the conventional heats of formation are the basic quantities employed.

Heats of Formation, Atomization, and Combustion

Thermochemical data are generally quoted in terms of heats of formation, Q_f, which are the heats liberated when one mole of the substance is produced from the elements in their standard states, viz., gaseous hydrogen, oxygen, and nitrogen, and carbon in the form of graphite. The data at 25°C. are considerably more extensive than those at any other temperature (including 0°K.), and in the present paper data at this temperature will always be used.

For the present purposes the most convenient procedure, and certainly the most fundamental, is to make use of heats of atomization, Q_a, instead of the heats of formation. By the heat of atomization (which will again always be referred to 25°C.) is meant the work required to dissociate one mole of the substance into its constituent atoms in their ground states. In the present paper heats of atomization have been calculated from heats of formation by making use of the following thermochemical relationships, which apply at 25°C.:

$$C_{graphite} = C_{gaseous}(^3P) - 171.7 \text{ kcal.},$$
$$\tfrac{1}{2}H_2 = H - 52.09 \text{ kcal.},$$
$$\tfrac{1}{2}O_2 = O - 59.16 \text{ kcal.},$$
$$\tfrac{1}{2}N_2 = N - 113.0 \text{ kcal.}$$

Of these values all except the last are taken from the National Bureau of Standards tables (46), which are the source of most of the thermochemical data employed here. The second and third values are well established on the basis of spectroscopic and other results, but the first and last have been the subject of considerable controversy and can still not be said to have been firmly established. On the whole, in the author's opinion, the evidence seems to point fairly strongly to the values quoted. The value given for graphite is consistent with the direct determination of the heat of sublimation of graphite by Brewer, Gilles, and Jenkins (8), and with some more recent work (10, 18). Springall (33) (see also Laidler and Casey (23)) has reviewed the evidence and favors this value. The nitrogen value given above was first proposed by Gaydon (14), and has been supported by much later work (13, 17, 21, 43).

On the basis of the above relationships it is easily seen that heats of atomization are related to heats of formation by the formula

$$[1] \qquad Q_a = Q_f + 171.7n_C + 52.09n_H + 59.16n_O + 113.0n_N$$

where n_C, n_H, n_O, and n_N are the numbers of carbon, hydrogen, oxygen, and

nitrogen atoms in the molecule. Heats of formation are frequently calculated from heats of combustion, Q_c, the two being related (for a compound containing only C, H, O, and N) by

[2] $$Q_f = -Q_c+94.05n_C+34.16n_H.$$

This formula assumes the combustion to give rise to carbon dioxide and nitrogen, and water in the liquid state. It is consistent with the thermochemical values given in the N. B. S. tables, namely

$$Q_c(\text{graphite}) = 94.05, \qquad Q_c(H_2\ \text{gas}) = 68.32.$$

The above two relationships give rise to

[3] $$Q_a = -Q_c+265.75n_C+86.25n_H+59.16n_O+113.0n_N.$$

The Bond Strength

The bond strength is a measure of the strength of the bond as it exists in the molecule, and its value is assigned in a purely empirical manner so that the sum of the various bond strengths in a molecule is equal to the heat of atomization. The present paper is concerned with the problem of assigning bond strengths in a self-consistent manner.

With diatomic molecules the bond strength is equal to the dissociation energy. In a polyatomic molecule containing only one type of bond, such as methane, there is again no difficulty; the bond strength is simply the heat of atomization divided by the number of bonds. For molecules containing more than one type of bond, on the other hand, the bond strengths cannot be defined with such precision. The procedure in such cases is to devise a scheme of classifying bonds that will give rise to a self-consistent scheme for all the molecules for which there are adequate data; a value is assigned to each type of bond in such a manner that the sum of the bond strengths is equal to the heat of atomization in every case. In the simplest schemes, such as those of Pauling (26) and Syrkin (37), all bonds connecting the same pair of atoms are considered to be the same. By taking into account all sorts of interactions it is apparent that very complicated schemes can be developed. From the most practical point of view it is evident that the most useful scheme is one that combines simplicity with accuracy. The system proposed in the present paper is a very simple one in that a differentiation between bonds connecting the same pair of atoms is only made in the case of carbon–hydrogen bonds, which are classified into different types which are readily recognized. In the present state of thermochemical data (which as far as homologous series are concerned are very incomplete except for the hydrocarbons) it is doubtful whether a more elaborate scheme would be justified or would give more satisfactory agreement with the data. As additional data accumulate, however, it will doubtless be advantageous to differentiate between bonds connecting other pairs of atoms; a scheme for doing this is in fact outlined below.

HEATS OF ATOMIZATION OF GASES

The N. B. S. tables (46) include values for heats of formation of a considerable number of paraffins, olefins, acetylenes, and aromatic compounds.

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With other classes of compounds, however, such as alcohols and nitrates, data for only a few scattered compounds are generally available. A more complete analysis can obviously be made for the former groups of compounds, and the bond strengths derived from these will be the backbone of the present system. The homologous series will be considered first, after which some values will be derived for bonds such as C–OH and C–ONO_2. The latter values will be subject to revision as more reliable and complete data become available.

The Paraffins

The inadequacy of the simple additive scheme for the paraffins, with all C–H bonds considered as the same, is readily demonstrated. Thus the bond strength in CH_4 is 398.0/4 = 99.5 kcal., and the assumption that this remains the same in ethane gives a C–C strength of 79.1 kcal. These values lead to a heat of atomization for *n*-hexane of 1788.5 kcal., whereas the observed value is 1799.5 kcal. The errors become greater as the size of the molecule increases.

The simplest way to effect some improvement is to classify carbon–hydrogen bonds as primary, secondary, and tertiary bonds. A primary bond is one that involves a carbon atom in common with two other C–H bonds (i.e. that appears in the structure $-CH_3$); a secondary bond is one that has a carbon atom in common with only one other C–H bond (in $>CH_2$); a tertiary bond is one that is alone (in $\gtrless CH$). A clue to how to improve the systems of bond additivities is provided by comparing, from this point of view, the heats of atomization of isomers. Thus in neopentane, in which all the C–H bonds are primary bonds, the heat of atomization is appreciably greater than that in the normal and iso compounds, and this suggests that primary bonds are stronger than secondary and tertiary ones; a similar conclusion can be drawn from the results for the two butanes.

In the light of this conclusion it is possible to proceed in a more quantitative manner and to arrive at a scheme which represents the heats to a considerably better approximation than does the simple procedure. This improved scheme will be built up on the basis of the following assumptions:

1. The strength of the C–C bond is the same in all of the paraffins; it may be denoted by c_1.

2. The strengths of all primary C–H bonds are the same; the strength may be denoted by p. Similarly the secondary and tertiary bond strengths, s and t, are constants.

There are four quantities, c_1, p, s, and t, to be determined from the data, and four Q_a values are therefore required to determine them. The success of the method depends upon what choice is made, and after the trial of a number of possibilities it was found that the most satisfactory agreement was obtained by using the values for 2,2-dimethylbutane, 3-methylhexane, 2,2-dimethylpentane, and 2,3-dimethylpentane. The data for these compounds give rise to the following equations:

$$5c_1+12p+2s = 1803.9, \quad [4]$$

$$6c_1+9p+6s+t = 2081.3, \quad [5]$$

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[6] $$6c_1+12p+4s = 2084.6,$$

[7] $$6c_1+12p+2s+t = 2082.9.$$

The solution of these equations gives

$$c_1 = 85.40 \text{ kcal.}, \qquad s = 97.650 \text{ kcal.},$$

$$p = 98.467 \text{ kcal.}, \qquad t = 96.797 \text{ kcal.}$$

Calculated Q_a values derived on the basis of these figures are shown in the fourth column of Table I, and the agreement is seen to be very satisfactory,

TABLE I

THE c_1–s–p–t SCHEME FOR THE PARAFFINS

c_1(C—C) = 85.40 p (primary C—H) = 98.467
s (secondary C—H) = 97.650 t (tertiary C—H) = 96.797

Paraffin	Bonds	Q_f (obs.)	Q_a (obs.)	Q_a (calc.)	Q_a(calc.) − Q_a(obs.)
Ethane, C_2H_6	c_1+6p	20.2	676.1	676.2	−0.1
Propane, C_3H_8	$2c_1+6p+2s$	24.8	956.6	956.9	−0.3
n-Butane, C_4H_{10}	$3c_1+6p+4s$	30.15	1237.85	1237.6	0.25
Isobutane, C_4H_{10}	$3c_1+9p+2s+t$	32.15	1239.85	1239.2	0.65
n-Pentane, C_5H_{12}	$4c_1+6p+6s$	35.0	1518.6	1518.3	0.3
Isopentane, C_5H_{12}	$4c_1+9p+2s+t$	36.9	1520.5	1519.9	0.6
Neopentane, C_5H_{12}	$4c_1+12p$	39.7	1523.3	1523.2	0.1
n-Hexane, C_6H_{14}	$5c_1+6p+8s$	39.96	1799.5	1799.0	0.5
2-Methylpentane, C_6H_{14}	$5c_1+9p+6s+t$	41.66	1801.2	1800.6	0.6
3-Methylpentane, C_6H_{14}	$5c_1+9p+6s+t$	41.02	1800.5	1800.6	−0.1
2,2-Dimethylbutane, C_6H_{14}	$5c_1+12p+2t$	44.35	1803.9	1803.9	0
2,3-Dimethylbutane, C_6H_{14}	$5c_1+12p+2t$	42.49	1802.0	1802.2	−0.2
n-Heptane, C_7H_{16}	$6c_1+6p+10s$	44.89	2080.2	2079.7	0.5
2-Methylhexane, C_7H_{16}	$6c_1+9p+6s+t$	46.6	2081.9	2081.3	0.6
3-Methylhexane, C_7H_{16}	$6c_1+9p+6s+t$	45.96	2081.3	2081.3	0
3-Ethylpentane, C_7H_{16}	$6c_1+9p+6s+t$	45.34	2080.6	2081.3	−0.7
2,2-Dimethylpentane, C_7H_{16}	$6c_1+12p+4s$	49.3	2084.6	2084.6	0
2,3-Dimethylpentane, C_7H_{16}	$6c_1+12p+2s+2t$	47.6	2082.9	2082.9	0

the errors* being in no case higher than 0.05%. Methane is not included, the C–H bond strength in it, 99.5 kcal., being greater again than that of a primary C–H bond.

In addition to the agreement with the observed Q_a values, the c_1–p–s–t scheme obtained in this way shows a number of other satisfactory and interesting features, as follows.

1. *Regularity of Values*

In the first place, the values for C–H (methane), C–H (p), C–H (s), and C–H (t) diminish in a more or less regular manner. A similar type of decrease in dissociation energies has frequently been invoked to explain the fact that in hydrocarbon chemistry the reactivity of C–H bonds decreases in the order

$$\text{tertiary} > \text{secondary} > \text{primary}.$$

Rice (28), for example, found the relative rates of attack of alkyl radicals on

Greater errors are, however, found with the octanes.

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primary, secondary, and tertiary hydrogen atoms to be 1:3:33 at 300°C. A similar conclusion has been reached from studies of the oxidation of hydrocarbons (48).

2. *Relationship with Heats of Dissociation*

The value obtained in the above manner for the C–C bond strength is consistent with that obtained by entirely independent methods for the *dissociation energy* of C–C bonds. Kistiakowsky and co-workers (1, 2, 22, 47) have shown that at 25°C. the heat of dissociation of methane into CH_3+H is ~102 kcal., and from this together with the thermochemical relationships

$$H_2 + C_2H_6 = 2CH_4 + 15.6 \text{ kcal.},$$

$$2H = H_2 + 104.2 \text{ kcal.},$$

it follows that

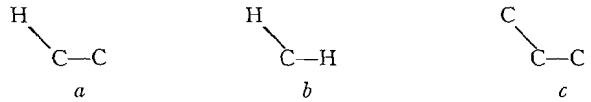
$$C_2H_6 = 2CH_3 - 84.4 \text{ kcal.}$$

This value, which is independent of the value for the heat of sublimation of carbon, is very close to the C–C bond strength obtained above ($c_1 = 85.40$). It is of interest that the c_1 value *is* dependent on the value assumed for the heat of sublimation of carbon; if the value of 125 kcal. were taken for this value, as proposed by some, c_1 would be 55.8 and therefore in considerable disagreement with the value for the heat of dissociation.

An interesting result is obtained when one derives from the present work a value for the heat of sublimation of diamond. Diamond can be considered to be an extended paraffin hydrocarbon, containing only C–C bonds, and the heat of sublimation of a mole should be the sum of the bond strengths for all of the bonds contained in a mole of carbon atoms. The number of bonds in a mole of diamond is twice the number of carbon atoms, so that the energy of sublimation should be $2\times85.40 = 170.8$ kcal. The experimental value is 171.2 kcal., in excellent agreement. No such agreement is obtained if bond strengths are calculated on the basis of other values for the heat of sublimation of graphite. Thus if the heats of atomization of all the paraffins had been calculated using the 125 kcal. value, the C–C bond strength (c_1) would have been 55.8 kcal. This leads to a heat of sublimation of diamond of $2\times55.8 = 111.6$ kcal., to be compared with the value for diamond of about 125 kcal. which must be assumed if the 125 value is taken for graphite.* This argument would appear to provide some evidence in favor of the 171 kcal. value.

3. *The Scheme of Near-neighbor Interactions*

It is now of interest to see how the scheme proposed is related to an alternative scheme that has some quantum-mechanical justification (9, 12), namely a scheme that takes into account interactions between bonds that spring from a common carbon atom. In the paraffins there are three different kinds of such interactions, and these may be denoted by *a*, *b*, and *c* as follows:



**The heat of sublimation of graphite is actually 0.45 kcal. greater than that of diamond.*

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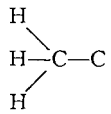
It would clearly be possible to attempt a scheme of bond strengths by assigning basic values g and h to the C–C and C–H bonds, respectively, and adding correction terms according to the numbers of interactions of the types a, b, and c. Such a scheme will be referred to as the g–h–a–b–c system.

Now it is readily seen that whenever there is a triplet of primary bonds, i.e. whenever the structure



exists, there are three interaction terms of type a, three of type b, and none of type c. Thus we have

$$3p = 3h+3a+3b. \quad [8]$$

In a similar manner it can be seen that

$$2s = 2h+4a+b+c \quad [9]$$

and

$$t = h+3a+3c. \quad [10]$$

These equations can be used to relate the c_1–s–p–t system to the g–h–a–b–c system. For example 3-methylpentane may be represented by either

$$5c_1+9p+4s+t$$

or

$$5g+14h+20a+11b+5c,$$

these alternative formulations being rendered equivalent by equations [8], [9], and [10].

It follows that there is no real difference between the two schemes, and that the c_1–s–p–t one is entirely consistent with the hypothesis that near-neighbor interactions are the only ones that need be considered. For practical purposes the c_1–s–p–t system is to be preferred, for various reasons. It is simpler to use, not only because it has one fewer parameter (four instead of five), but because it is easier to count bond types than bond interactions. Furthermore, if the g–h–a–b–c system is used one of the values must be assigned entirely arbitrarily. That this is so may be seen by inserting into eqs. [8], [9], and [10] the p, s, and t values obtained earlier, and attempting to solve for h, a, b, and c. Since there are three equations and four unknowns this cannot be done, but one can arrive at the solutions

$$c = -0.018,$$

$$2a-b = -1.616.$$

One may assign a purely arbitrary value to either a or b, after which it is possible to proceed. Suppose that b is arbitrarily given the value zero; it follows that

$$a = -0.808.$$

One finds that

$$h = 99.275.$$

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The conclusion is that a g–h–a–b–c scheme with the values

$$g = 85.40, \quad a = -0.808,$$
$$h = 99.275, \quad b = 0,$$
$$c = -0.018$$

(or indeed an infinite number of other schemes with a or b chosen arbitrarily) is equivalent to the c_1–p–s–t scheme proposed above, and will give exactly the same predictions for the heats of atomization of the paraffins.

The Olefins

The unsaturated hydrocarbons can be treated in a somewhat similar manner. After trials of various possibilities it has been found that the most satisfactory procedure for the olefins is to classify carbon–hydrogen bonds as follows:

(1) Bonds that are neither next to, nor next but one to, a double bond; these are considered to be ordinary primary, secondary, and tertiary bonds and to have the bond strengths calculated above for the paraffins.

(2) Bonds that are next but one to a double bond; these may be primary, secondary, or tertiary bonds, and their strengths are denoted as p', s', and t'.

(3) Bonds that are next to a double bond; these may be secondary or tertiary and their strengths will be denoted as s_2 and t_2. The carbon–carbon single bond strength (c_1) is assumed to be the same as previously determined; the carbon–carbon double-bond strength will be denoted as c_2.

In order to determine the additional bond strengths c_2, p', s', t', s_2, and t_2, the following heats of atomization were chosen:

(1) 3-Methyl-1-butene
$3c_1+c_2+6p+2s_2+t_2+t' = 1386.3$

(2) 2-Methyl-2-butene
$3c_1+c_2+t_2+9p' = 1389.6$

(3) 2-Methyl-1-butene
$3c_1+c_2+3p+2s_2+3p'+2s' = 1388.1$

(4) 4-Methyl-1-pentene
$4c_1+c_2+6p+t+2s_2+t_2+2s' = 1667.0$

(5) 2-Ethyl-1-butene
$4c_1+c_2+6p+2s_2+4s' = 1668.2$

(6) 3,3-Dimethyl-1-butene
$4c_1+c_2+9p+2s_2+t_2 = 1669.6$

With the values obtained earlier for c_1, p, s, and t, these equations give rise to the figures given in Table II. In Table III are shown calculated and observed values for a large number of olefins; the agreement is seen to be very satisfactory.

TABLE II

BOND STRENGTHS FOR C—C AND C—H BONDS

$c_1 = 85.40$	$p = 98.467$	$p' = 98.902$	
$c_2 = 145.275$	$s = 97.650$	$s' = 98.002$	$s_2 = 99.2575$
	$t = 96.797$	$t' = 97.483$	$t_2 = 98.007$

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TABLE III

CALCULATED AND OBSERVED HEATS OF ATOMIZATION FOR OLEFINS

Compound	Bonds	Q_f (obs.)	Q_a (obs.)	Q_a (calc.)
Ethylene	c_2+4s_2	−12.50	539.3	542.3
Propylene	$c_1+c_2+t_2+2s_2+3p'$	− 4.88	822.8	823.9
1-Butene	$2c_1+c_2+t_2+2s_2+2s'+3p$	+ 0.03	1103.6	1104.0
cis-2-Butene	$2c_1+c_2+2t_2+6p'$	1.67	1105.2	1105.5
trans-2-Butene		2.67	1106.2	1105.5
2-Methylpropene	$2c_1+c_2+2s_2+6p'$	4.04	1107.5	1108.0
1-Pentene	$3c_1+c_2+t_2+2s_2+2s'+2s+3p$	5.00	1384.4	1384.7
cis-2-Pentene	$3c_1+c_2+2t_2+2s'+3p'+3p$	6.71	1386.1	1387.4
trans-2-Pentene		7.59	1387.0	1387.4
2-Methyl-1-butene	$3c_1+c_2+2s_2+2s'+3p'+3p$	8.68	1388.1	1388.1
3-Methyl-1-butene	$3c_1+c_2+t_2+t'+2s_2+6p$	6.92	1386.3	1386.3
2-Methyl-2-butene	$3c_1+c_2+t_2+9p'$	10.17	1389.6	1389.6
1-Hexene	$4c_1+c_2+t_2+2s_2+2s'+4s+3p$	9.96	1665.3	1665.4
cis-2-Hexene	$4c_1+c_2+2t_2+2s'+2s+3p'+3p$	11.56	1666.9	1666.3
trans-2-Hexene		12.56	1667.9	1666.3
cis-3-Hexene	$4c_1+c_2+2t_2+4s'+6p$	11.56	1666.9	1665.7
trans-3-Hexene		12.56	1667.9	1665.7
2-Methyl-1-pentene	$4c_1+c_2+2s_2+2s'+2s+3p+3p'$	13.56	1668.9	1668.8
3-Methyl-1-pentene	$4c_1+c_2+t_2+t'+2s_2+2s+6p$	11.02	1666.4	1667.2
4-Methyl-1-pentene	$4c_1+c_2+t_2+t+2s_2+2s'+6p$	11.66	1667.0	1667.0
2-Methyl-2-pentene	$4c_1+c_2+t_2+2s'+6p'+3p$	14.96	1670.3	1667.0
cis-3-Methyl-2-pentene	$4c_1+c_2+t_2+2s'+6p'+3p$	14.32	1669.6	1669.7
trans-3-Methyl-2-pentene		14.32	1669.6	1669.7
cis-4-Methyl-2-pentene	$4c_1+c_2+2t_2+t'+3p'+6p$	13.26	1668.6	1667.9
trans-4-Methyl-2-pentene		14.26	1669.6	1667.9
2-Ethyl-1-butene	$4c_1+c_2+2s_2+4s+6p$	12.92	1668.2	1668.2
2,3-Dimethyl-1-butene	$4c_1+c_2+2s_2+t'+3p'+6p$	14.78	1670.1	1670.4
3,3-Dimethyl-1-butene	$4c_1+c_2+2s_2+t_2+9p$	14.25	1669.6	1669.6
2,3-Dimethyl-2-butene	$4c_1+c_2+12p'$	15.91	1671.2	1673.7

TABLE IV

ACETYLENIC COMPOUNDS

Compound	Bonds	Q_f (obs.)	Q_a (obs.)	Q_a (calc.)	Q_a(calc.) − Q_a(obs.)
Acetylene, $CH\equiv CH$	c_3+2t_3	−54.2	393.4	394.9	1.5
Methylacetylene, $CH_3C\equiv CH$	$c_3+c_1+t_3+3p$	−44.3	679.2	679.4	0.2
Ethylacetylene $C_2H_5\equiv CH$	$c_3+2c_1+t_3+2s+3p$	−39.7	959.6	960.1	0.5
Dimethylacetylene, $CH_3C\equiv CH_3$	c_3+2c_1+6p	−35.4	963.9	963.9	0
Propylacetylene, $C_3H_7C\equiv CH$	$c_3+3c_1+t_3+4s+3p$	−34.5	1240.7	1240.8	0.1
Methylethylacetylene, $CH_3C\equiv CC_2H_5$	$c_3+3c_1+2s+6p$	−30.8	1244.4	1244.6	0.6
Isopropylacetylene $CH_3CH(CH_3)C\equiv CH$	$c_3+3c_1+t_3+6p+t$	−32.6	1242.6	1242.4	−0.2
n-Butylacetylene $C_4H_9C\equiv CH$	$c_3+4c_1+t_3+6s+3p$	−29.6	1521.5	1521.5	0
n-Pentylacetylene, $C_5H_{11}C\equiv CH$	$c_3+5c_1+t_3+8s+3p$	−24.6	1802.4	1802.2	−0.2
n-Hexylacetylene, $C_6H_{13}C\equiv CH$	$c_3+6c_1+t_3+10s+3p$	−19.7	2083.2	2082.9	−0.3
n-Heptylacetylene, $C_7H_{15}C\equiv CH$	$c_3+7c_1+t_3+12s+3p$	−14.8	2363.9	2363.6	−0.3

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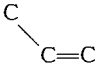
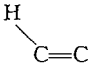
It may be seen that one source of minor error in the treatment arises from the neglect of forces between non-bonded atoms. That these forces are significant is illustrated by the differences in heats of atomization between *cis* and *trans* isomers; thus *cis*-2-pentene and *trans*-2-pentene, although having identical bond systems, have heats differing by 0.9 kcal. Generally the *trans* compound has the higher value, but the 3-methyl-2-pentenes (see Table III) constitute an exception.

Relationship to a Scheme of Interactions

It is now of interest to see how the scheme proposed is related to an interaction scheme. The double bond introduces the two following additional neighboring-bond interactions:

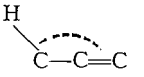


d



e

Since, moreover, bonds next but one to a double bond are found to be slightly different from *p*, *s*, and *t* bonds, it is clear that the interaction



f

is also involved. The following relationships are then obtained:

[11] $$t_2 = h+a+e+d,$$

[12] $$2s_2 = 2h+b+2e,$$

[13] $$3p' = 3h+3a+3b+3f,$$

[14] $$2s' = 2h+4a+b+c+2f,$$

[15] $$t' = h+3a+3c+f.$$

Insertion into eqs. [11] and [12] of the known values of t_2, s_2, h, a, and b gives rise to

$$d = -0.4425, \qquad e = -0.0175.$$

Insertion into eq. [13] of the values of p', h, a, and b gives rise to

$$f = 0.435.$$

A similar treatment of eqs. [14] and [15] gives values for f of 0.343 and 0.632. Equations [13], [14], and [15] are not exactly compatible, but are nearly so, and a slightly different set of values for p', s', and t' would lead to equal values of f. The scheme proposed is therefore very closely similar to (but is much simpler than) an interaction scheme of the type indicated.

It is of interest that whereas the interactions c, d, and e (and perhaps a and b also) are all negative, the f interaction is positive; this is of course related to the fact that C–H bonds are slightly strengthened by being next but one to double bonds.

The Acetylenes

Column 2 of Table IV lists heats of formation for a number of acetylenes, and these have been converted into heats of atomization in column 3.

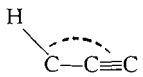
The best agreement was obtained by using the following values:

$$c_3 \text{ (the C}\equiv\text{C bond strength)} = 202.3 \text{ kcal.},$$

t_3 (the strength of a C–H bond adjacent to a triple bond) = 96.3 kcal.

The Q_a values calculated on this basis are shown in the fourth column. It was found that no advantage was gained by employing special values for C–H bonds next but one to the triple bond; the regular p, s, and t values are used for these.

This scheme is evidently equivalent to one of neighboring-bond interactions, the next-near-neighbor interaction



being taken to be zero. The interaction term corresponding to

$$\text{H—C}\equiv\text{C}$$

is $96.3 - 99.275 = -2.975$ kcal.

Aromatic Compounds

Observed heats of formation and of atomization of aromatic compounds are shown in Table V. In the fourth column are given heats of atomization

TABLE V

AROMATIC COMPOUNDS

Compound	Bonds	Q_f	Q_a (obs.)	Q_a (calc.)	Q_a(calc.) $-Q_a$(obs.)
Benzene, C_6H_6	$3c_1+3c_2+6t_2$	−19.8	1322.9	1280.1	42.8
Toluene, $CH_3C_6H_5$	$4c_1+3c_2+5t_2+3p'$	−11.9	1606.7	1564.2	42.5
Ethylbenzene, $C_2H_5C_6H_5$	$5c_1+3c_2+5t_2+2s_1+3p$	−7.1	1887.4	1844.3	43.1
o-Xylene, $(CH_3)_2C_6H_4$	$5c_1+3c_2+4t_2+6p'$	−4.5	1890.0	1848.3	41.7
m-Xylene, $(CH_3)_2C_6H_4$	$5c_1+3c_2+4t_2+6p'$	−4.1	1890.4	1848.3	42.1
p-Xylene, $(CH_3)_2C_6H_4$	$5c_1+3c_2+4t_2+6p'$	−4.3	1890.2	1848.3	41.9
n-Propylbenzene, $C_3H_7C_6H_5$	$6c_1+3c_2+2s'+2s+3p+5t_2$	−1.9	2168.5	2125.0	43.5
Isopropylbenzene, $C_3H_7C_6H_5$	$6c_1+3c_2+5t_2+6p+t'$	−0.9	2169.5	2126.5	43.0
1-Methyl-2-ethylbenzene, $CH_3(C_2H_5)C_6H_4$	$6c_1+3c_2+4t_2+2s'+3p+3p'$	−0.3	2170.1	2128.4	41.7
1-Methyl-3-ethylbenzene, $CH_3(C_2H_5)C_6H_4$	$6c_1+3c_2+4t_2+2s'+3p+3p'$	−0.5	2170.9	2128.4	42.5
1-Methyl-4-ethylbenzene, $CH_3(C_2H_5)C_6H_4$	$6c_1+3c_2+4t_2+2s'+3p+3p'$	0.8	2171.2	2128.4	42.8
1,2,3-Trimethylbenzene, $(CH_3)_3C_6H_3$	$6c_1+3c_2+3t_2+9p'$	2.3	2172.7	2132.4	40.6
1,2,4-Trimethylbenzene, $(CH_3)_3C_6H_3$	$6c_1+3c_2+3t_2+9p'$	3.3	2173.7	2132.4	41.3
1,3,5-Trimethylbenzene, $(CH_3)_3C_6H_3$	$6c_1+3c_2+3t_2+9p'$	3.8	2174.2	2132.4	41.8
					Av. = 42.2

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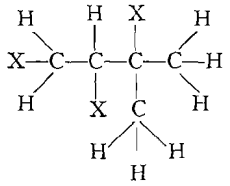
calculated without regard to resonance energy, i.e., by treating the double bonds in the benzene ring as ordinary double bonds. The differences between the observed and calculated values are listed in the last column, and are seen to be quite constant. The average value of these differences is 42.2 kcal., and this can be taken to be the resonance energy, the value of which should be subtracted when it is desired to estimate the heats of atomization or formation of benzene derivatives.

Compounds Containing Specific Groups

It is now necessary to consider the situation when hydrogen atoms in the hydrocarbons are replaced by specific groups, such as aldehyde, alcohol, and nitrate groups. This type of compound cannot, in principle, be treated in as simple a manner as previously, and unfortunately a completely satisfactory system of bond energies cannot as yet be worked out. This is because there do not exist, in the case of compounds containing specific groups, data for a sufficient number of homologous compounds. It is, however, of interest to consider a general type of treatment that it will ultimately be possible to test using adequate data. Two situations may be considered; the one in which there is no more than one of the specific groups X on any carbon atom, and the one in which more than one group is present. The latter situation is more complex in that interactions of the type X—C—X must be considered.

1. When there is never more than one X on each carbon atom, as in the compound



it may be seen that as far as neighbor interactions are concerned all possible structural features of the compound are included in a scheme that recognizes three different types of C–X bonds:

(*a*) bonds in which X replaces a primary hydrogen atom; these may be designated x^p bonds;

(*b*) x^s bonds, in which a secondary hydrogen atom is replaced; and

(*c*) x^t bonds, involving a tertiary hydrogen.

Since the values of c_1, p, s, t, etc., have been determined from the hydrocarbon data, it would be possible to evaluate x^p, x^s, and x^t from the data for those members of a homologous series of this type, and to test the system on additional members of the series. For an adequate test it would be desirable to have data for at least 10 compounds, and the data should be accurate to within 0.2 kcal. or so. Neither of these conditions can as yet be satisfied for any group X.

2. When more than one X can be on a carbon atom the simplest scheme taking into account neighbor interactions would be one in which they are

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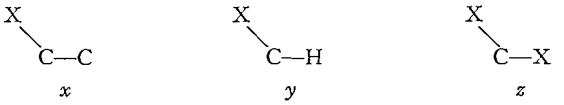
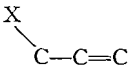
treated explicitly. A theory of this type would proceed as follows. The additional interaction terms are



with more being necessary if there are double or triple bonds; in the former case it would probably be desirable to add terms for the next-near-neighbor interaction



The interaction terms a, b, c, d, and e have already been calculated from the hydrocarbon data, and results for these compounds containing C–X bonds would enable x, y, and z to be determined. Again this cannot as yet be done for lack of adequate data.

In view of the fact that data do not permit a treatment equivalent to that for the hydrocarbons the best that can at present be done is to treat all C–X bonds as equivalent, and be content with bond strengths that are an average of values showing some scatter. For most practical purposes this procedure is in fact adequate, since most compounds of interest contain only a few C–X bonds; the errors therefore do not tend to accumulate in the way they do with C–H bonds.

This procedure has been applied to a number of different groups, and the contributions of various groups to the energy of atomization have been evaluated. Since the data for substances other than the hydrocarbons are not very accurate or extensive the details will not be given here. A note on the sources of the thermochemical values is given in the Appendix, and the final group contributions are shown in Table VI. The procedure used in

TABLE VI

RECOMMENDED CONTRIBUTIONS FOR SPECIFIC GROUPS

Bond	Contribution to heat of atomization, kcal.
C—OH (alcohol)	198.1
C—O—C (ether)	172.0
C—CHO (aldehyde)	355.4
C—CO—C (ketone)	350.1
C—COOH (acid)	480.1
C—NH_2 (amine)	256.6
C—NO_2 (nitro)	285.2
C—ONO_2 (nitrate)	354.5

deciding the type of a C–H bond is to treat the substituent as if it were a carbon atom; in ethyl alcohol, for example, it is considered that there are three primary C–H bonds and two secondaries. An alternative procedure would be to consider all five to be primaries, since the molecule is derived from ethane, which has six primaries. The procedure employed seems to give a smaller spread of values.

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There is a great need for additional work on series of homologous compounds, and the values given in Table VI will require revision as new data accumulate.

HEATS OF VAPORIZATION

The bond contributions arrived at in the previous section enable an estimate to be made of the heats of atomization of gases and, by an extension to be discussed later, of the heats of formation and combustion of gases. It is clearly of some practical importance to be able to extend this system to liquids and solids. In the present section a start has been made on this problem for the case of liquids; for solids a satisfactory solution will probably have to await further experimental results.

The procedure that has been adopted is to analyze data for heats of vaporization and to arrive at a scheme of bond energies of the same type as that used for heats of atomization. It is then a simple matter to combine the two systems and so obtain a scheme of bond energies for liquids; this is done in the section that follows.

It is actually found that heats of vaporization are not strictly additive in terms of bonds, and that for best agreement the presence of certain structural features (such as five–carbon structures of the neopentane type) should be taken into account. However the simple system of bond energies is, as will be seen, very satisfactory, and is certainly adequate for present purposes. Since heats of vaporization are relatively small compared with heats of atomization and combustion (and sometimes with heats of formation) a large percentage error in a heat of vaporization will lead to only small errors in the final estimated values.

Paraffins

Accurate values for a number of paraffins are given in the N. B. S. tables (46), and some of them are shown in the second column of figures in Table VII. Analysis of these values reveals the fact that it is possible to make

TABLE VII

CALCULATED AND OBSERVED HEATS OF VAPORIZATION FOR PARAFFINS

Paraffin	Heat of vaporization (kcal. per mole)		Difference (calc. − obs.)
	Obs.	Calc.	
n-Hexane	7.540	7.596	0.056
2-Methylpropane	4.570	4.967	0.397
2-Methylbutane	5.878	6.125	0.247
2-Methylpentane	7.138	7.186	0.048
2-Methylhexane	8.318	8.444	0.126
2-Methylheptane	9.483	9.602	0.119
2-Methyloctane	10.670	10.760	0.090
3-Ethylpentane	8.419	8.441	0.022
3-Ethylhexane	9.475	9.599	0.124
3-Ethylheptane	10.710	10.757	0.047
2,2-Dimethylpropane	5.200	5.932	0.732
2,2-Dimethylbutane	6.617	7.080	0.363
2,2-Dimethylpentane	7.751	8.238	0.487
2,2-Dimethylhexane	8.912	9.396	0.484
2,2-Dimethylheptane	10.100	10.554	0.454

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reasonable estimates of them using the following values for the contributions of the various bonds:

$$c_1 = 0 \text{ kcal.}, \qquad s = 0.579 \text{ kcal.},$$

$$p = 0.494 \text{ kcal.}, \qquad t = 0.518 \text{ kcal.}$$

Table VII shows calculated values and the differences between calculated and observed. The agreement is seen to be reasonably satisfactory in most cases, but is least so in hydrocarbons having the neopentane type of structure; such compounds have heats of vaporization that are significantly lower than the predicted ones, a fact that may be related to their high degree of symmetry. In estimating the values for compounds containing this structural feature it would be well to subtract a value of about 0.5.

The data for unsaturated hydrocarbons are unfortunately not adequate to allow a similar treatment to be applied to them.

Compounds Containing Specific Groups

Heat of vaporization data for compounds such as alcohols, ethers, and acids are not extensive and not of great accuracy. Application of the same type of treatment as the above, however, leads to the conclusion that to a useful approximation the values are additive. This is illustrated by the results shown in Table VIII for the nitrates; the data for these are fairly reliable (see Appendix). The details for other groups will not be given, but the thermochemical data employed are discussed in the Appendix and the final group contributions are summarized in Table IX.

TABLE VIII

HEATS OF VAPORIZATION OF NITRATES

Nitrate	Q_s (obs.)	C—ONO_2
CH_3ONO_2	8.2	6.72
$C_2H_5ONO_2$	8.7	6.06
CH_2ONO_2 | CH_2ONO_2	15.7	6.69
CH_2ONO_2 | $CHONO_2$ | CH_2ONO_2	21.7	6.29
		Av. 6.44

Improvement for all of these compounds could no doubt be achieved by employing a procedure such as that used by Wiener (50), who introduces parameters that take some account of the general shape of the molecule. However for present purposes it is more useful to have a system that is of the same type as that used for heats of atomization—i.e. involving only bond contributions. With such a system for heats of vaporization it is then possible,

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as will now be explained, to arrive at a scheme for making predictions of the thermochemical values for liquids.

TABLE IX

BOND CONTRIBUTIONS TO HEATS OF VAPORIZATION

Bonds	Contribution (kcal. per mole)
C—C	0
C—H (*p*)	0.494
C—H (*s*)	0.579
C—H (*t*)	0.518
C—OH	6.76
C—CHO	5.21*
C—CO—C	6.76
C—O—C	1.25
C—COOH	18.8*
C—ONO_2	6.44
C—NO_2	7.04

**Based on one heat of vaporization only; data from Ref. (35).*

TABLE X

BOND CONTRIBUTIONS FOR HEATS OF ATOMIZATION, FORMATION, AND COMBUSTION OF GASES AND LIQUIDS

Bond	Symbol	Heat of atomization		Heat of formation		Heat of combustion	
		Gas	Liquid	Gas	Liquid	Gas	Liquid
C—C	c_1	85.4	85.4	−0.45	−0.45	47.48	47.48
C=C	c_2	145.3	(145.3)	30.2	(30.2)	32.5	(32.5)
C≡C	c_3	202.3	(202.3)	−55.3	(−55.3)	196.3	(196.3)
C—H	p	98.47	98.96	3.45	3.95	54.22	53.73
C—H	s	97.65	98.23	2.64	3.21	55.04	54.46
C—H	t	96.80	97.32	1.78	2.30	55.89	55.37
C—H	p'	98.90	(99.40)	3.89	(4.38)	53.79	(53.29)
C—H	s'	98.00	(97.58)	2.99	(3.57)	54.69	(54.11)
C—H	t'	97.48	(98.00)	2.47	(2.99)	55.20	(54.69)
C—H	s_2	99.26	(99.84)	−10.07	(−9.49)	75.58	(75.00)
C—H	t_2	98.01	(98.53)	−25.62	(−24.11)	98.97	(98.45)
C—H	t_3	96.30	(96.82)	1.29	(1.80)	56.39	(55.87)
C—OH	a_{lc}	198.1	204.9	49.93	50.69	13.75	6.99
C—O—C	e	172.0	173.3	27.0	28.3	20.0	18.7
C—CHO	a_{ld}	355.4	360.6	29.5	34.7	122.2	117.0
C—CO—C	k	350.1	356.9	33.4	40.2	107.7	100.9
C—COOH	a_c	480.1	498.6	95.1	113.9	56.7	37.9
C—NH_2	a_m	256.6	—	−3.5	—	95.3	—
C—NO_2	n_i	285.2	292.2	11.0	18.0	12.6	5.5
C—ONO_2	n_a	354.5	361.0	21.1	27.5	2.4	−4.0
C—$NHNO_2$	n_{m1}	—	440.2	—	0.9	—	56.8
C>NNO_2 C	n_{m2}	—	421.3	—	−8.9	—	55.9

The values in brackets are based on the assumption that the contributions for the heats of vaporization of C—H are the same irrespective of the proximity of double and triple bonds.

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HEATS OF FORMATION AND COMBUSTION OF GASES AND LIQUIDS

In the present section the results of the previous work will be consolidated and an outline will be given of a complete set of procedures for estimating heats of atomization, formation, and combustion of both gases and liquids.

Table X shows the final bond contributions that have been arrived at. The methods used in obtaining them will now be discussed.

Heats of Atomization

The first column of numbers in the table consists of the values obtained earlier. The second shows the corresponding values for liquids. Since both the heats of atomization and the heats of vaporization are given additively in terms of bond contributions it is necessary simply to add together the two contributions in order to obtain that for the heat of atomization of a liquid. For example, the value 361.0 for the nitrate group is the sum of 354.5, the gas contribution, and 6.5, that for the heat of vaporization.

Heats of Formation

The conventional heat of formation is related to the heat of atomization by eq. [1], which involves n_C, n_H, n_O, and n_N, the numbers of the various atoms in the molecule. In order to relate the contributions for heats of formation to those for heats of atomization it is necessary to relate n_C, n_H, n_O, and n_N to the numbers of the various bonds in the molecule.

The following example will illustrate the type of procedure that may be employed for doing this. Consider a molecule containing C_1 carbon–carbon single bonds, C_2 carbon–carbon double bonds, P primary (p) C–H bonds, S secondary (s) C–H bonds, S_2 bonds of type s_2 (next to a double bond), T_2 bonds of type t_2 (next to a double bond), S' bonds of type s', N_a nitrate groups, and A_{ld} aldehyde groups. According to the previous work (see column 1 of Table X) the heat of atomization of such a compound in the gas phase will be

$$[16]\quad Q_a = 85.4\ C_1+145.28\ C_2+98.47\ P+97.65\ S+99.26\ S_2 +98.00\ S' +354.5\ N_a+355.4\ A_{ld}.$$

If n_C, n_H, n_O, and n_N can be expressed in terms of C_1, C_2, P, etc., it will then be possible to express Q_f as a linear function of C_1, C_2, P, etc., with explicit coefficients that will be the relevant bond contributions for the various atoms and groups.

Consider first the number of carbon atoms, n_C, in the molecule under consideration. The presence of a primary C–H bond implies the existence of a carbon atom, but since the carbon atom is tetravalent the bond actually only has a one-fourth share in it;* for each primary C–H one must therefore count only a quarter of a carbon atom. The same argument applies to secondary (and tertiary) C–H bonds, and to bonds next but one to a double bond. We thus find that

$$[17]\quad n_C = \tfrac{1}{4}(P+S+S')+ \ldots .$$

**This is no longer true if the C—C bond is next to a double or triple bond; the correction required for this is considered later.*

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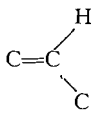
Each C–C single bond has a fourth share in two carbon atoms, so that

[18] $$n_C = \tfrac{1}{4}(P+S+S')+\tfrac{1}{2}C_1+ \ldots .$$

Each C–ONO_2 bond has a fourth share in a carbon atom, while each aldehyde group has a fourth share in one carbon atom and a full share in another; thus

[19] $$n_C = \tfrac{1}{4}(P+S+S')+\tfrac{1}{2}C_1+\tfrac{1}{4}N_a+\tfrac{5}{4}A_{1d}+ \ldots .$$

A slight complication arises from the presence of double (and triple) bonds. Each C=C double bond has one-third share in two carbon atoms, so that the contribution is $\frac{2}{3}C_2$ (for a triple bond it is C_3). An S_2 bond has one-third share in a carbon atom, so that the contribution is $\frac{1}{3}S_2$. Similarly a t_2 bond has a one-third share in a carbon atom, so that a contribution of $\frac{1}{3}T_2$ is indicated. However this result neglects one factor. The existence of a t_2 bond implies the structure*



and this means that an error has been made in treating the C–C single bond, since one end of this is a carbon atom that is only attached to three different atoms. The contribution at one end of the carbon atom is therefore $\frac{1}{3}$ rather than $\frac{1}{4}$, and the estimated number of carbon atoms is therefore too low by $\frac{1}{3}-\frac{1}{4} = \frac{1}{12}$ for every time this structure appears. The easiest way to make the correction is to add a term $\frac{1}{12}T_2$. The final expression for the number of carbon atoms in the molecule is therefore

[20] $$n_c = \tfrac{1}{4}(P+S+S')+\tfrac{1}{2}C_1+\tfrac{2}{3}C_2+\tfrac{1}{3}S_2+(\tfrac{1}{3}+\tfrac{1}{12})T_2+\tfrac{1}{4}N_a+\tfrac{5}{4}A_{1d}.$$

Proceeding in a similar manner for the various bonds it is possible to arrive at the coefficients shown in the first column of Table XI. The procedure for the remaining bonds is straightforward except when triple bonds are present. Here again the contributions from C–C single bonds will be wrongly counted unless a correction is made. The number of times the structure

C—C≡C

appears in a molecule is $2C_3-T_3$, and every time it appears the number of carbon atoms is in error by $\frac{1}{4}$; the term $\frac{1}{4}(2C_3-T_3)$ must therefore be added. The expression for n_C for a molecule containing triple bonds therefore contains the terms

[21] $$n_C = C_3+\tfrac{1}{2}T_3+\tfrac{1}{4}(2C_3-T_3)+ \ldots .$$

The second column of figures in Table XI shows the corresponding coefficients in the expression for n_H, while the third and fourth are for n_O and n_N. These are obtained in a similar way to the coefficients for n_C.

A special treatment is required if one of the substituent groups is next to the double bond. There are, however, few data for this type of compound.

TABLE XI

MATRIX OF COEFFICIENTS WHICH RELATE n_C, n_H, n_O, AND n_N TO THE NUMBERS OF BONDS

Bond	n_C	n_H	n_O	n_N
C_1	$\frac{1}{2}$	0	0	0
C_2	$\frac{2}{3}$	0	0	0
C_3	2	0	0	0
P	$\frac{1}{4}$	1	0	0
S	$\frac{1}{4}$	1	0	0
T	$\frac{1}{4}$	1	0	0
P'	$\frac{1}{4}$	1	0	0
S'	$\frac{1}{4}$	1	0	0
T'	$\frac{1}{4}$	1	0	0
S_2	$\frac{1}{3}$	1	0	0
T_2	$\frac{5}{12}$	1	0	0
T_3	$\frac{1}{4}$	1	0	0
A_{1c}	$\frac{1}{4}$	1	1	0
E	$\frac{1}{2}$	0	1	0
A_{1d}	$\frac{5}{4}$	1	1	0
K	$\frac{3}{2}$	0	1	0
A_c	$\frac{5}{4}$	1	2	0
A_m	$\frac{1}{4}$	2	0	1
N_i	$\frac{1}{4}$	0	2	1
N_a	$\frac{1}{4}$	0	3	1
N_{m1}	$\frac{1}{4}$	1	2	2
N_{m2}	$\frac{1}{2}$	0	2	2

In order to obtain the bond contribution to the heat of formation one proceeds as follows. The expression for Q_f contains a number of terms, that for the nitrate group, for example, being as follows:

$$[22] \quad Q_f = Q_a - 171.7\ n_C - 52.09\ n_H - 59.16\ n_O + 113.0\ n_N$$

$$[23] \quad = 354.5\ N_a + \ldots - 171.7\ (\tfrac{1}{4}N_a + \ldots) - 52.09(0 + \ldots) - 59.16(3N_a + \ldots) - 113.0(N_a + \ldots)$$

$$[24] \quad = 21.10\ N_a + \ldots .$$

The entry in the third column of numbers in Table X for the nitrate group is therefore 21.10. The remaining figures are obtained in a similar way.

The values for the liquid state are obtained in the same manner as for the heats of atomization, making use of the heat of vaporization contributions.

Heats of Combustion

The heat of combustion is related to the heat of formation by eq. [2]. The bond contributions to the heats of combustion can therefore be calculated from those for the heats of formation by making use of the appropriate coefficients in Table XI, the procedure being similar to the above. The heat of vaporization contributions must now be *subtracted* from the gas values to obtain those for the liquids.

The resulting contributions are shown in the last two columns of Table X.

SOME EXAMPLES

In order to illustrate the method, and to give some indication of its reliability, typical calculations will now be carried out.

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Ethyl Nitrate

The calculation of the heat of combustion of liquid ethyl nitrate is as follows:

$$\begin{aligned} 1 \times c_l &= 47.48 \\ 3 \times p &= 161.19 \\ 2 \times s &= 108.92 \\ 1 \times n_a &= -4.0 \end{aligned}$$

$$Q_c = 313.59 \text{ kcal.}$$

The observed value, derived from Berthelot's heat of esterification of ethyl nitrate and from Gray's treatment of Wheeler, Whittaker, and Pike's explosion data, is 313.2 kcal.

The heat of formation calculation is, for the liquid:

$$\begin{aligned} 1 \times c_l &= -0.45 \\ 3 \times p &= 11.85 \\ 2 \times s &= 6.42 \\ 1 \times n_a &= 27.5 \end{aligned}$$

$$Q_f = 45.32 \text{ kcal.}$$

The observed value, based on the data referred to above, is 45.7 kcal.

Diethyl Nitramine

The heat of combustion of liquid diethyl nitramine is calculated as follows:

$$\begin{aligned} 2 \times c_l &= 94.96 \\ 6 \times p &= 322.38 \\ 4 \times s &= 217.84 \\ 1 \times n_{m2} &= 55.9 \end{aligned}$$

$$Q_c = 691.08 \text{ kcal.}$$

The observed value is 692.2 ± 0.9 kcal.

ACKNOWLEDGMENTS

The author is grateful to Dr. Peter Gray and Mr. Harold Hurwitz for discussions relative to the thermochemistry of the nitrates, and to Dr. Theodore Austin for work on the heats of vaporization. He is also indebted to Miss Susan Pyatt and Mrs. O. Kracek for help with the computations and for valuable suggestions.

APPENDIX. SOURCES OF THERMOCHEMICAL DATA

Hydrocarbons

Q_f and Q_v data were obtained in all cases from the N. B. S. tables (46).

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Alcohols

Q_f values for *n*-alcohols up to C_{10} from Rossini (31); other values quoted by Bischowsky and Rossini (6) and by Roberts and Skinner (30).

Q_v values from Landolt-Börnstein (24).

Ethers

Q_f values from Bischowsky and Rossini (6), Kharasch (20), and Stohmann (34). Q_v values calculated from vapor pressure data of Stull (35).

Aldehydes

Q_f values for formaldehyde and acetaldehyde only (46). Q_v values calculated from vapor pressure data of Stull (35).

Ketones

Roberts and Skinner (30) quote Q_f values for CH_3COCH_3, $C_2H_5COCH_3$, *n*-$C_3H_7COCH_3$, and *sec*-$C_3H_7COCH_3$. Q_v values for the first three were calculated from Stull's vapor pressure data (35); Q_f(gas) for the last was obtained using an estimated Q_v. The four Q_f values employed were 51.8, 58.2, 65.1, and 66.8 kcal., respectively.

Acids

Q_f values for HCOOH, CH_3COOH, $CH_2ClCOOH$, and $CHCl_2COOH$ are given by Bischowsky and Rossini (6). A C–Cl value of 80.5 was assumed. Q_v's calculated from Stull's data (35).

Amines

Reliable Q_f data appear to be available only for methylamine and ethylamine (46). No reliable Q_v values.

Nitro Compounds

Thermochemical data for nitro compounds are not of high reliability. Some Q_f values for liquids are given in the Landolt-Börnstein tables (24) and were converted into gaseous values using either experimental heats of vaporization (6) or values estimated using the methods of this paper. Bischowsky and Rossini (6) give Q_v values for nitromethane and nitroethane.

Nitrates

Some of the data for the nitrates are contradictory; discussion of the individual compounds is therefore necessary.

Methyl Nitrate

The value of 29.0 kcal. for Q_f(gas) is based upon a value of Q_f(liquid) = 37.2 kcal. calculated by Gray and Smith (16) from heat of explosion data of Wheeler, Whittaker, and Pike (49), and a heat of vaporization of 8.2 kcal. calculated from vapor pressure measurements of McKinley-McKee and Moelwyn-Hughes (25).

Other sources of data are as follows. Swientoslawski (36) quotes Berthelot as having obtained Q_c(gas) = 166.2, presumably on the basis of the heat of esterification. Using modern thermochemical data this leads to Q_f(liquid) = 39.1. In view of the uncertain origin of this value, however, that of Gray seems

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preferable. An alternative determination of Q_v is due to Thompson and Purkis (44), whose results lead to 7.8 kcal. On the whole the McKinley-McKee and Moelwyn-Hughes value seems more reliable; the vapor pressures were measured over a wider temperature range, and the results were fitted to the Antoine equation (Thompson and Purkis report their results only as the equation of a straight line on a log p vs. $1/T$ graph).

Ethyl Nitrate

A value for Q_f(liquid) of 45.7 was calculated by Gray (15) from Wheeler, Whittaker, and Pike's heat of explosion data (49), and the same value is obtained by applying modern auxiliary data to Berthelot's heat of esterification value (5). Thomsen (45) obtained different results by measuring Q_c directly, but the error in this type of investigation is intrinsically greater than in heat of esterification measurements. In view of this, and of the agreement between Berthelot and Gray, their value seems preferable (16*a*).

The vapor pressure of ethyl nitrate was measured by Goodeve (14*a*) over a range of temperature, and a reanalysis of her data leads to a value of $Q_v = 8.7$ at 25°C.

These values lead to Q_f(gas) = 37.0.

Glycol Dinitrate

Rinkenbach (29) and Schmidt (32) give Q_c(liquid) values that both lead to Q_f(liquid) = 58.2. A value of $Q_v = 15.7$ comes from vapor pressure results of Brandner (7); when fitted to the Antoine equation they lead to 15.7 at 25°C. Crater (11) carried out a similar study, but his data lead to a higher Q_v. For various reasons Brandner's results seem more reliable.

Nitroglycerine

A Q_f(liquid) value of 89.0 is calculated from Taylor and Hall's value (41) of 364 for Q_c(liquid). A variety of earlier values have been given in the literature, and Taylor and Hall list objections to these, based mainly on defects in experimental procedures or on absence of information.

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THE FORMATION OF SUPERCOOLED LIQUID SOLUTIONS IN SIMPLE-EUTECTIC TYPE ORGANIC SYSTEMS BY THE SUBLIMATION OF SOLID MIXTURES[1]

By Ralph H. Petrucci[2] and C. H. Sorum[3]

ABSTRACT

A process is described for the formation of supercooled liquid solutions by the sublimation of solid mixtures—the liquids formed being supercooled in the sense that they can be condensed from the vapor phase above solid mixtures at temperatures below the eutectic values. The process can be thought of as proceeding, solids → mixed vapor → supercooled liquid solutions. The general nature of this phenomenon in organic systems of the simple-eutectic type is established as a result of the microscopic and macroscopic experiments performed in this investigation. A $P/T/c$ space-model of a typical binary, eutectic-type, organic system, *o*-nitrophenol–naphthalene, is presented. A physical picture of the process under consideration is made possible on the basis of this model.

INTRODUCTION

In an earlier contribution from this laboratory, Sorum and Durand (4) reported the fact that individual crystals, maintained out of physical contact, could melt at temperatures just slightly above their eutectic temperature as a result of the condensation of the vapor phase above them. Forty-five organic, binary, eutectic-type systems were studied at that time and this phenomenon was observed in every case.

In the present work it was noted that condensation to liquids occurred even when solids were maintained at temperatures below their eutectics. In order that liquids might condense it was necessary to have the collecting surfaces at temperatures below those of the solids; the entire systems therefore were at temperatures below the eutectic values. The liquids formed under these conditions were supercooled solutions of the two components; the evidence of supercooling was the fact that these liquids persisted at temperatures below the eutectics. The present paper is concerned with some of the factors involved in the formation of supercooled liquids by this process.

EXPERIMENTAL

A. Materials

All the chemicals used in this investigation were organic compounds of relatively low melting points and high vapor pressures (*ca.* 10^{-4} to 10^{-1} mm.). The compounds were recrystallized twice from suitable solvents, dried for one to two days over appropriate desiccants in a vacuum desiccator, and then further dried at elevated temperatures and reduced pressures in an Abderhalden Drying Apparatus. The melting points and melting point ranges of the final products were used as criteria of purity.

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B. Apparatus for Microscopic Experiments

A Bausch and Lomb crystallographic microscope, equipped with 8 and 16 mm. objectives and 7.5 and 10× eyepieces, was used for all the microscopic work. Heating and thermostating of samples were accomplished by the use of a water-heated microscope hot-stage fabricated from aluminum metal. A small water bath equipped with heaters, cooling coils, bimetallic thermoregulator, and circulating pump served as a source of water. The stage could be thermostated with a precision of a few tenths °C. By continuously varying the temperature of the external bath, heating and cooling rates from 0.1° to 1.0°C. per minute could be established. Accurately calibrated mercury-in-glass thermometers inserted through a re-entrant thermometer well were used for making temperature measurements in the stage. A set of inserts fitting into the central light orifice made the stage adaptable for all of the various microscopic measurements—melting points, eutectic temperatures, refractive indices, sublimation temperatures, etc.

C. Macroscopic Sublimation Apparatus

Macroscopic studies on the condensation of liquid sublimate from the vapor phase above solid mixtures were carried out in an all-glass sublimation apparatus. The essential features of this apparatus were sublimation wells to hold the solid samples and "cold-thumb" condensers (maintained at a short distance above the solids) upon which sublimate could condense.

Macroscopic sublimation studies were performed on the system *o*-nitrophenol–naphthalene. Solid mechanical mixtures of the two components were placed in the sublimation wells of the sublimation apparatus and thermostated at one temperature. By maintaining the "cold-thumb" condensers of the apparatus at some lower temperature, liquid condensates were collected on the condensers. Collection of the condensates was allowed to continue for a few days and when sufficient amounts of liquid had deposited (*ca.* 0.01–0.05 ml.) these liquids were analyzed by a microscopic refractometric method.

D. Determination of Eutectic Temperatures

The eutectic temperature for a multicomponent system is the equilibrium temperature at which all the phases, solid, liquid, and vapor, are present in bulk. In practice to initiate and maintain a finite rate of freezing the temperature of a system must be somewhat below the eutectic temperature. To initiate and maintain melting the temperature must be slightly above the eutectic. The true eutectic temperature is somewhere between these upper and lower limits. For the purposes of this paper the melting temperature has been taken as essentially equal to the equilibrium temperature.

Two microscopic methods were used in establishing eutectic temperatures. One was the "contact-method" developed by the Koflers (2). The second method simply involved crystallizing liquid samples between 12- and 25-mm. microscope cover glasses and then observing the lowest temperature at which fusion occurred when these samples were slowly reheated. In contrast to the "contact-method" where eutectic fusion occurred only in a limited "zone-of-mixing" of the components, with the "fusion-preparations" eutectic fusion

could take place anywhere in the crystalline area. The latter method proved to be particularly applicable to studies on ternary and quaternary systems where "zones-of-mixing" of all the components were difficult to establish.

E. Refractive Index Measurements

Mixtures of *o*-nitrophenol and naphthalene were analyzed by determining the refractive indices of solutions of the two components. A series of "working-curves" was established, giving the temperatures at which mixtures of fixed composition had specified refractive indices. Compositions of unknown mixtures were obtained by referring to these standard curves. This method is described in detail by the Koflers (2). Refractive index curves for the system *o*-nitrophenol–naphthalene are presented in Fig. 1.

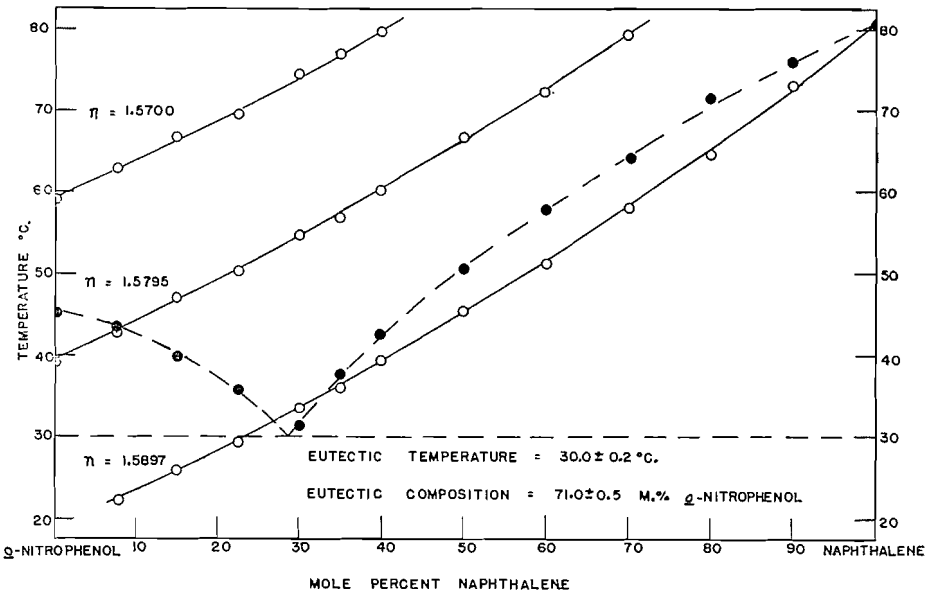

FIG. 1. Equilibrium diagram (closed circles) and refractive index curves (open circles) for the system *o*-nitrophenol–naphthalene.

STUDIES ON THE SYSTEM *o*-NITROPHENOL–NAPHTHALENE

A. Determination of the Equilibrium Diagram

The equilibrium diagram for the system, *o*-nitrophenol–naphthalene, was determined by a combination of macroscopic and microscopic methods. The macroscopic method used was essentially the "thaw-point" method of Rheinboldt (3). In this procedure synthetic solid mixtures are prepared and the melting of such samples followed in a conventional capillary melting-point type of apparatus. The pertinent data are the "beginning melting point" and the "end melting point". In this system the "beginning melting point" for every sample was the eutectic temperature. The "end melting point" corresponded to the primary crystallization temperature in a cooling curve study on a binary system. The synthetic mixtures required were obtained by

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melting together weighed amounts of the two components sufficient to give a solution of a few milliliters volume. These solutions were then crystallized and carefully pulverized in a cold mortar. The resulting solid mixtures were used for the melting point determinations. Microscopic melting points were also determined on samples prepared in this same manner.

The equilibrium diagram for the system, *o*-nitrophenol–naphthalene, based on macroscopic melting points is presented in Fig. 1. Equilibrium relationships are shown by dashed lines. Refractive index curves for the system, plotted on the same temperature and composition scales, are given as solid lines.

B. Subeutectic Region of the P/T/c Space-model

The space-model (see Fig. 2) for this system was calculated principally from literature data, although two items of experimental information from this investigation, the eutectic temperature and eutectic composition, were also required. In Fig. 2 the curve *LK* is the vapor pressure curve for pure solid naphthalene and *JI* the vapor pressure curve for pure solid *o*-nitrophenol. The curves *HN* and *GM* define the sum of the vapor pressures of the two

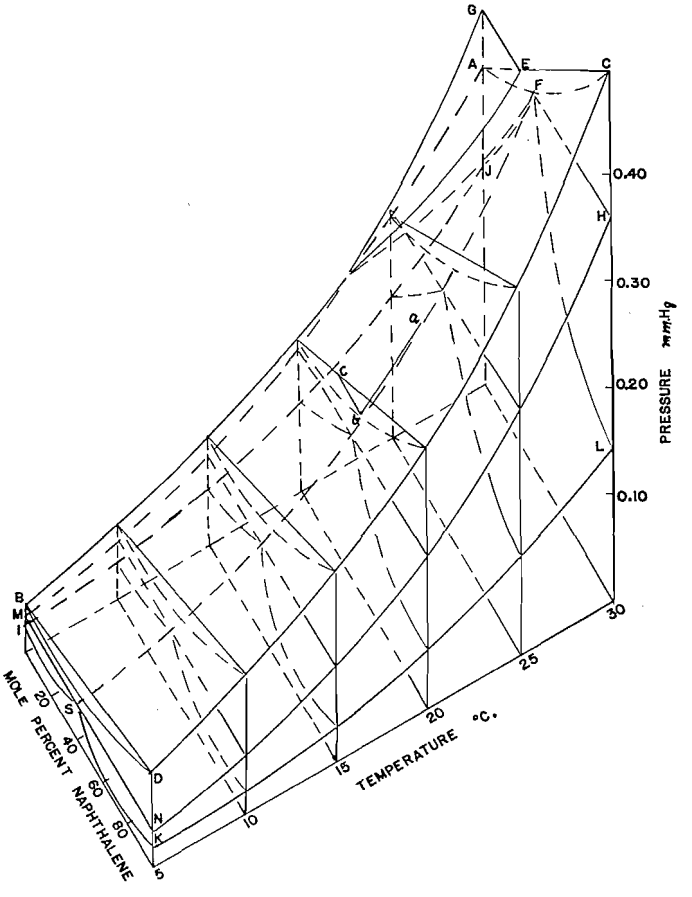

FIG. 2. A perspective drawing of a portion of the *P/T/c* space-model for the system *o*-nitrophenol–naphthalene.

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solids as a function of temperature. The surface *GMNH* is a ruled surface generated by an infinite collection of isobaric, isothermal tie lines. The mole ratio of the two components in the vapor phase above solid mixtures at any temperature is equal to the ratio of the vapor pressures of the pure solids at that temperature, if the vapors are assumed ideal. Variation of vapor composition with temperature is given by the curve *FS*.

Because no vapor pressure data for solid *o*-nitrophenol could be found in the literature and because the existing vapor pressure data for solid naphthalene were not altogether consistent, vapor pressure values for the solid components were calculated from a knowledge of liquid vapor pressures. Liquid vapor pressures were obtained from Stull's compilation (5). The heat of vaporization of each pure liquid was calculated from a conventional log p vs. $1/T$ plot. Heats of fusion of the two solids were available in the literature (1). The sum of the heat of vaporization and the heat of fusion for each component at its triple point was taken as the heat of sublimation for that component. By extrapolating the liquid vapor pressure data to temperatures below the melting points of the respective components, a value of the vapor pressure for each supercooled liquid at the eutectic temperature was obtained. An assumption was then made that Raoult's law was obeyed by the eutectic liquid, and from this law a value for the vapor pressure was derived for each pure solid at 30°C. Substituting these vapor pressures and the previously derived heats of sublimation into the Clausius–Clapeyron equation, a vapor pressure equation for each solid component was established. The vapor pressure equations employed were: for solid *o*-nitrophenol, $\log p(\text{mm.}) = -3634/T+11.32$ (*a*) and for solid naphthalene, $\log p(\text{mm.}) = -3516/T+10.71$ (*b*).

The variation of vapor pressure with temperature for supercooled liquid naphthalene is shown in Fig. 2 by the curve *CD*. *AB* is the vapor pressure curve for supercooled liquid *o*-nitrophenol. The supercooled liquid–vapor equilibrium surface was obtained by again assuming the validity of Raoult's law for solutions of *o*-nitrophenol and naphthalene.

C. Discussion

The process by which vapors generated above solid mixtures condense to yield supercooled liquid solutions can be illustrated with reference to the space-model. If we consider a simple experiment in which a mixture of the solids *o*-nitrophenol and naphthalene is held at one temperature in a sublimation well of the sublimation apparatus and a "cold-thumb" condenser at some lower temperature, the following phenomena can occur: First of all the mixed vapor arising from the solids at the higher temperature can simply condense to give a mixture of solids. It is also possible, however, for the vapor, as it is cooled, to pass from the solid–vapor surface without condensing into solids. If this vapor is cooled to a sufficient extent, the point in space representing the variables of state of the vapor phase will strike the vaporous surface of the supercooled liquid–vapor loop and at this point a liquid can condense. With reference to Fig. 2 these steps are represented by the points *a*, *b*, and *c*. A solid mixture vaporized at the temperature of point *a* yields a vapor phase whose composition is also fixed by point *a*. (The point *a* lies on the dashed line

FS.) This vapor then cools in some fashion (pressure may decrease in this cooling process because of the existence of a temperature gradient between condenser and solids) until its representative point in space strikes the vaporous surface of the supercooled liquid–vapor loop at point *b*. At this point vapor may condense yielding a liquid condensate of composition *c*.

If such an experiment is performed where the solid mixture is held at the eutectic temperature and the condenser at a temperature only very slightly below this, then the model shows that eutectic vapor, *F*, will condense to give essentially the eutectic liquid, *E*.

The model of Fig. 2 is strictly applicable only to systems where *o*-nitrophenol and naphthalene are the sole substances present. However as the effect of external pressure on equilibrium between condensed phases is usually quite small, the exertion of an additional atmosphere of pressure on these solids would leave their vapor pressures essentially unchanged. This means that the vapor composition and total vapor pressure above a solid mixture in a system open to the atmosphere should be practically identical to the corresponding quantities in a closed system with air excluded. In all the experimental work solid mixtures were maintained at atmospheric pressure. Preliminary experiments were performed which showed that the composition of the liquid collected in the process, solids → mixed vapor → supercooled liquid solutions, was unaffected by external pressure in the range from *ca.* 1 to 760 mm.

Other preliminary experiments were conducted to test the effect of the composition of the solid mixtures on the composition of the supercooled solutions condensed from the vapor phase. As might be expected for a system of the simple-eutectic type, a type of system characterized by complete immiscibility of the solid components, the compositions of the liquid condensates were independent of the compositions of the solid mixtures from which they were ultimately derived.

Studies on the effect of the temperature variable consisted in thermostating the condensers of the sublimation apparatus at a particular set of temperatures and then determining, to within a few tenths of a degree, the temperatures to which solid mixtures had to be heated in order for the first liquid sublimate to form on the condensers. A period of a few hours was allowed at each temperature before a higher temperature was tried. The results of these studies are tabulated in Table I.

TABLE I

LIQUID SUBLIMATE FORMATION AS A FUNCTION OF TEMPERATURE IN THE SYSTEM *o*-NITROPHENOL–NAPHTHALENE

Temperature of solid mixture, °C.	Temperature of condenser, °C.	Composition of the liquid sublimate, mole % *o*-np
29.0	28.4	71.0
28.5	27.5	71.0
27.0	25.5	71.0
25.5	23.5	71.5
24.0	21.5	72.5
23.0	19.5	73

Eutectic composition for this system: 71.0 mole % o-nitrophenol. Precision of the analyses: 0.5–1 mole % o-nitrophenol.

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The first feature that can be brought out from Table I is arrived at by comparing the first and second columns in that table. It is seen that at the higher solid temperatures only small temperature differences had to be maintained between the sublimation wells and condensers in order for liquid sublimate to form. At lower temperatures the required temperature differences became progressively greater. These temperature differences, considered as a function of temperature, indicate the manner in which the two surfaces, solid–vapor and liquid–vapor, are oriented with respect to each other in the composition region along the dashed line *FS* of Fig. 2.

The variation of the composition of liquid sublimate with the temperatures of generation and condensation of mixed vapors is seen in the third column of Table I. It is noted that at higher temperatures eutectic liquid was formed and that at lower temperatures a trend was established in the direction of somewhat higher concentrations of *o*-nitrophenol in the liquid sublimate. Though the difference in composition of the liquid at the highest and lowest temperatures was slight, it was still felt to be outside the range of experimental error.

Calculations stemming from equations (*a*) and (*b*) indicate that at the eutectic temperature the composition of the vapor in equilibrium with solid *o*-nitrophenol and naphthalene should be about 60 M.% *o*-nitrophenol and should increase to about 62–63 M.% *o*-nitrophenol at temperatures of 5° or 10°C. Constant-temperature cross-sections of the space-model for the temperature range from 30° to 10°C. were constructed and from these cross-sections the compositions of the liquid in equilibrium with a vapor containing 60 M.% *o*-nitrophenol were estimated. For example, the estimated liquid composition at 30°C. was 71 M.% *o*-nitrophenol; at 10°C., 74 M.% *o*-nitrophenol.

From these considerations we can see that even if vapor composition in this system did not change with temperature, we should expect a slight change in liquid composition, increasing percentages of *o*-nitrophenol in the liquid at the lower temperatures. Add to this effect the possibility of a slight enrichment of the vapor phase in *o*-nitrophenol content at lower temperatures and it is all the more to be expected that some change in liquid composition should occur with decreasing temperature of liquid formation.

MICROSCOPIC STUDIES

In order to investigate a large number of systems and thus to prove the general nature of the phenomenon, solids → mixed vapor → supercooled liquid solution, rapid semiquantitative microscopic methods were employed. The microscopic studies served to show that supercooled liquids could be condensed from the vapor phase in a number of systems of the unary, binary, ternary, and quaternary types.

In the microscopic sublimation studies mixtures containing approximately equal weights of all the components of a system of a given type were first prepared. Samples of these mixtures were placed on a 12-mm. cover glass maintained at one level in the sublimation chamber insert of the microscopic hot-stage. At a level about 3 to 4 mm. above the solids a 25-mm. cover glass was supported. The stage was heated at a rate of 0.2°C. per minute and the

lower surface of the upper cover glass was observed microscopically during the heating process. The lowest temperature at which a microscopically visible liquid deposit appeared was recorded; this temperature was called the liquid sublimation temperature. Also for each system a number of experiments were performed in which the solid components at the lower level were maintained out of physical contact. In some cases, after a liquid sublimate had started to form, the temperature of the stage was maintained at a constant value for a period of time and larger quantities of supercooled liquids were thereby collected. These liquids were crystallized at dry ice temperatures and the resulting crystallized samples observed upon reheating.

DISCUSSION

Representative data obtained in these microscopic studies are compiled in Table II. A number of interesting observations can be drawn from these data. It is noted first of all that in every case liquid was obtained at tempera-

TABLE II

MICROSCOPIC DATA FOR THE FORMATION OF LIQUID SUBLIMATES

System type	System	Melting point, °C.	Eutectic temperature	Liquid sublimation temperature,* °C.
Unary	Acenaphthene	93.6	—	>60
	Azobenzene	67.4	—	51.2
	Benzil	95.0	—	>60
	Naphthalene	80.0	—	57.9
	α-Nitronaphthalene	56.9	—	44.3
	o-Nitrophenol	44.9	—	36.4
	p-Nitrophenol	113	—	>60
Binary	*o*-Nitrophenol Naphthalene	44.9 80.0	30.0	27.8[a]
	Azobenzene Naphthalene	67.4 80.0	41.8	35.0[b]
	α-Nitronaphthalene Naphthalene	56.9 80.0	35.1	29.8[c]
	α-Nitronaphthalene Azobenzene	56.9 67.4	35.8	30.9
	o-Nitrophenol Azobenzene	44.9 67.4	28.7	28.3
	Azobenzene Acenaphthene	67.4 93.6	48.6	38.5[d]
	Acenaphthene Benzil	93.6 95.0	63.9	57.3[e]
	Azobenzene Benzil	67.4 95.0	52.5	41.6[f]
	Azobenzene *p*-Nitrophenol	67.4 113	49	48.5

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TABLE II (*concluded*)

System type	System	Melting point, °C.	Eutectic temperature	Liquid sublimation temperature,* °C.
Ternary	*o*-Nitrophenol Azobenzene Naphthalene	44.9 67.4 80.0	18.6	16.2[g]
	α-Nitronaphthalene Azobenzene Naphthalene	56.9 67.4 80.0	21.6	19.6[h]
	Azobenzene Acenaphthene Benzil	67.4 93.6 95.0	37.8	35.5[i]
	Acenaphthene Benzil *p*-Nitrophenol	93.6 95.0 113	50	46.5
	Azobenzene Acenaphthene *p*-Nitrophenol	67.4 93.6 113	44.4	38.0
	Azobenzene Benzil *p*-Nitrophenol	67.4 95.0 113	40.0	38.5
Quaternary	Azobenzene Acenaphthene Benzil *p*-Nitrophenol	67.4 93.6 95.0 113	32.0	30.5

Notes on the melting points of crystallized sublimates:
(a) Beginning melting point, 29.8°C., end melting point, 29.8°C.; (b) 42.0, 43.5; (c) 34.5, 35.5; (d) 47.3, 51; (e) 63, ca. 67; (f) 51, 53.5; (g) 17.5, 19.5; (h) crystallization incomplete, 24; (i) 37.4, 41.5.

**The temperature of the surroundings of the microscope stage was maintained at about 10° to 15°C. below the eutectic temperature for each sublimation study.*

tures below the lowest eutectic temperature. This observation was made both in the case of mixtures and for the "non-contact" studies. Except for small differences in liquid sublimation temperatures the phenomenon of condensation of supercooled liquid solutions above solids did not depend upon whether the solids were in physical contact.

The fact that in every case liquid formation in a binary system took place at a lower temperature than in either unary indicates that both components were present in the supercooled liquid in the binary system, since at these temperatures the vapor phase could not have been saturated with respect to either of the pure components. A similar situation existed in the ternary and quaternary systems.

In a number of experiments (see footnotes to Table II) a sufficient amount of liquid was collected to allow for a subsequent melting point determination on a crystallized sample. The fact that all preparations began to melt at or near the appropriate eutectic temperatures shows that each liquid sublimate

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must have contained all the components present in the original solid samples. (It is noted that in a few instances the "beginning melting point" for a recrystallized sample was somewhat below the indicated eutectic temperature. Here it is probable that crystallization was incomplete at dry ice temperatures. The "beginning melting point" simply signifies the temperature at which a solid phase began to disappear rapidly.)

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HYDROGEN OVERPOTENTIAL ON ALUMINUM[1]

By D. J. Hansen[2] and F. E. W. Wetmore

ABSTRACT

The hydrogen overpotential of pure and impure aluminum in 0.1 N H_2SO_4 at 25° has been studied. The effect of the autocorrosion of the metal has been interpreted and the role of impurities in determining the overpotential and the rest potential has been shown. As well, the build-up and decay of the overpotential has been studied; the behavior is much more complicated than that of noble metals.

Studies of hydrogen overpotential on aluminum have been few (2, 3, 5, 6, 7, 8) and in most cases details of procedure and the degree of purity of the metal are lacking or there is indication that proper experimental precautions (1) have not been taken. In no case was the rate of corrosion reported, although it may have been substantial. The investigation reported here was an exploration at low current densities, for which there are no serious doubts about the homogeneity of current density distribution.

EXPERIMENTAL

The electrolyte used for all experiments was 0.1 N H_2SO_4, a concentration selected as a compromise between the desires for high conductivity and low rate of corrosion. The water was of "conductivity" grade, $k = 8\times10^{-7}$ ohm^{-1} $cm.^{-1}$, the acid redistilled reagent quality. The electrolyte was purged with purified hydrogen and subjected to lengthy pre-electrolysis, according to the method recommended by Bockris and co-workers (1).

The aluminum cathode and platinum anode of the cell were in separate compartments connected through closed ungreased stopcocks wet with solution. Hydrogen was bubbled continuously about both electrodes. An auxiliary cathode of platinum was available for pre-electrolysis. A capillary probe near the cathode surface led to a reference electrode, 0.1 N H_2SO_4/Hg_2SO_4, Hg. Four types of cathode material were selected for study: (I) rolled sheet, 99.995% pure, (II) cast polycrystalline, 99.995% pure, (III) single crystal, 99.995% pure, and (IV) "commercially pure" ingot, 99.5% pure. The cathodes were electropolished in a perchloric acid bath, then mounted in a Teflon box which exposed only one flat face. Unless stated otherwise, current densities mentioned refer to the apparent area of this face.

The currents used were electronically regulated. The potential difference between the probe and cathode was passed to a direct-coupled amplifier of very high impedance (about 10^{13} ohms) and thence to a torsion string galvanometer (Model TSB-A29, Kipp en Zonen, Delft). The deflection of the galvanometer could be recorded on film in a drum camera. Alternatively, a potentiometer was used for steady state readings. Rates of corrosion were determined by measurement of the weight loss of the sample; a resistance–capacitance bridge

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Contribution from the Electrochemical Laboratory, University of Toronto, Toronto 5, Canada.
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was used to show that the resistance, and hence the thickness, of the oxide film did not change sufficiently to cause appreciable error in the weight loss measurements.

RESULTS AND DISCUSSION

In the following description the overpotential will be defined as the potential of the reversible hydrogen electrode in the electrolyte less the potential of the cathode, and will therefore be positive.

Figure 1A shows the overpotential plotted against the logarithm of the applied current density, i_x, for sample I; the curves for samples II and III

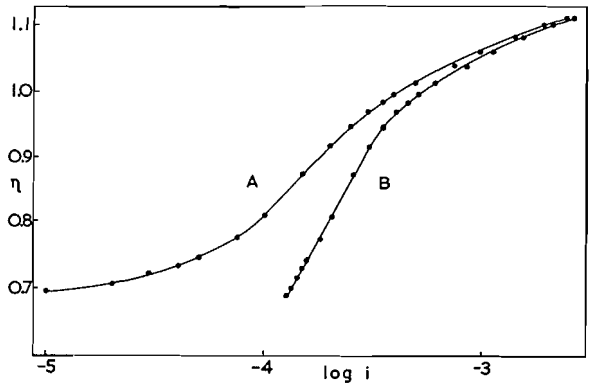

FIG. 1. Overpotential of sample I as a function of the applied current density (A) and the total current density (B).

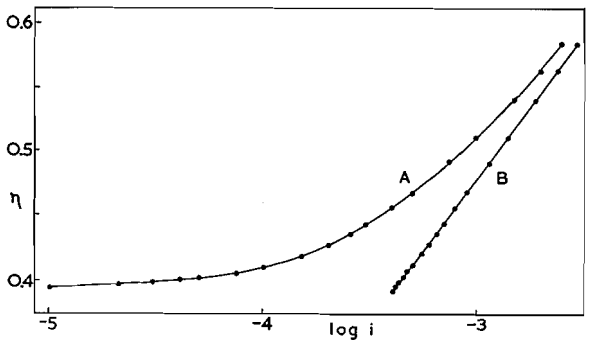

FIG. 2. Overpotential of sample IV as a function of the applied current density (A) and the total current density (B).

are similar. Figure 2A shows the curve for sample IV; it differs from the others in not exhibiting a bend to lower slope at the higher current densities. All of these curves show a distinct deviation from the linearity frequently found for unreactive metals, expressed by Tafel's relation

$$\eta = b \ln(i/i_0). \qquad [1]$$

Even when there is no applied current there is a cathodic current due to the autocorrosion of the sample. Under this condition the cathodic current I is

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identical with the corrosion current I_a. With application of an electrolyzing current I_x, the total cathodic current I equals I_a+I_x. Table I gives corrosion

TABLE I

CORROSION CURRENT DENSITIES AND REST POTENTIALS

Sample	I	II	II*	III	IV
i_a, μa.cm.$^{-2}$	25	28	22	33	103
E_r	0.675	0.650	0.640	0.625	0.368

**Second series, one month after first.*

current densities from weight loss determinations through Faraday's law. These data were obtained without applied current. Weight loss measurements made with electrolyzing current flowing showed that the corrosion current is enhanced by current densities above some 75 μa. cm.$^{-2}$. These corrosion rates were not as reproducible as those taken without electrolyzing current. Fortunately this is not a serious concern in determining $\log(i_a+i_x)$. For typical example, at $i_x = 267$ with $i_a = 50$, a deviation of 10 in i_a would represent only 0.015 in $\log(i_a+i_x)$. The curves B of Figs. 1 and 2 are plotted with $\log(i_a+i_x)$ as the abscissae. These curves show that at the lower current densities the overpotential is indeed linear in the logarithm of the *total* cathodic current density.

It was found that the rest potentials of the samples (E_r at $I_x = 0$) were diverse and were decreased after prolonged electrolysis. There exists, however, a relationship between the corrosion current density and the rest potential. This is shown in Table I; the rest potentials recorded were taken before prolonged electrolysis.

With the exception of sample IV, the cathodes showed a decrease in the slope of the "Tafel curve" at the higher current densities. Such a change in slope is sometimes attributed to a change in the mechanism of the discharge process. In this case an explanation of more direct appeal is to attribute the change to an alteration in the nature of the active cathodes. It will be assumed that both the aluminum and the traces of impurities present can act as cathodes. The total cathodic current I can then be visualized as consisting of two terms, I_1 for that part of the current accepted by the aluminum, and I_2 for that accommodated by the impurities. Thus

$$[2] \qquad I_a+I_x = I_1+I_2.$$

Spectroscopic analysis showed iron and copper to be the major part of the 0.005% of impurity present in samples I, II, and III. From earlier work (3) iron and copper are known to have low overpotentials at low current densities with marked rise at very high current densities. It is possible that these impurities can accommodate the greater part of the current at low current densities, even though their exposed areas are extremely minute, since the overpotential of the aluminum at very low current density may be greater than the overpotential of the impurities at the relatively high current densities

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corresponding to their small exposed areas. This, and the variation in the slope of curve B of Fig. 1, can be explained more formally in terms of the behavior of mixed cathodes.

Let b_1 denote the slope of the curve of overpotential of aluminum plotted against ln I_1. Then $b_1 = I_1(d\eta/dI_1)$. Similarly for the impurities, $b_2 = I_2(d\eta/dI_2)$. Further, let b^* denote the slope of the curve for the mixed cathodes (the actual experimental curve). Then $b^* = (I_1+I_2)[d\eta/d(I_1+I_2)]$. It follows that

$$[3] \qquad 1/b^* = I_1/b_1(I_1+I_2)+I_2/b_2(I_1+I_2) = \phi_1/b_1+\phi_2/b_2,$$

in which ϕ_1 is the fraction of the total cathodic current flowing to the aluminum and ϕ_2 that to the impurities. Thus it is seen that b^* becomes identical with b_1 only as ϕ_1 becomes much greater than ϕ_2. From the form of the curves B of Figs. 1 and 2, the impurities appear to be the predominant cathodes at the low current densities and b^* can be expected to approach b_1 only for high current density on very pure metal. Some confirmation of this viewpoint can be obtained from examination of the rest potentials of the samples (Table I). Sample IV contains one hundred times as much impurity as the other three; the ratio of the exposed areas of impurities will be about the same number. The current density of autocorrosion is therefore much less on the impurities of sample IV than on those of the other three; this is reflected in the much lower rest potential of sample IV. It is consistent with this observation to say that the rest potential is simply the overpotential on the impurities at the particular current density defined by the corrosion current and the area of the impurities exposed. This concept is supported by calculation of the value of the quotient: the difference between the rest potential of sample IV and that of another sample, divided by the natural logarithm of their current density ratio (taking into account the 100:1 ratio of areas of impurities). From Table I the values of the quotients range from 0.074 to 0.100, in agreement with those for iron and copper, but much too high for aluminum.

It is now clear why the rest potential varies without apparent change of conditions, why it varies with the proportion and kind of impurity, why it is affected by prolonged electrolysis, and why the overpotential decreases slightly with prolonged electrolysis. The rest potential is very sensitive to the area of impurites exposed, which can vary as aluminum is dissolved away. Even minute traces of ions of more noble metals present in the electrolyte, whether initially or by dissolution, can change the effective area of active cathode by plating out as the sample is driven cathodically. This emphasizes the need for high purity in both the aluminum and the electrolyte.

Although definite values for the parameters of the overpotential of aluminum cannot be stated from this work, it is evident that both b and i_0 of equation [1] must have very small values, even smaller than those previously reported. The determination of precise values will require the use of extremely pure metal at current densities as high as can be consistent with homogeneous distribution of the current. Work with zone-crystallized metal is proposed.

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Both build-up and decay of overpotential as functions of time were determined with the galvanometer and drum camera. For noble metals the initial and greater part of the potential-coulomb curve of build-up is linear; with aluminum cathodes the curve is not linear in any part, in agreement with the following considerations. The generally accepted theory of overpotential leads to an expression for the rise of potential with time of the form (4)

$$[4] \qquad dE/dt = I/C - K.\exp(E/b),$$

in which C is a constant with the dimensions of capacitance, K is a constant, and b is the slope of the "Tafel curve" (equation [1]). Before an electrolyzing current is applied there exists the steady state of rest potential, E_r, and the corrosion current, I_a. Equation [4] then becomes

$$[5] \qquad 0 = dE/dt = I_a/C - K.\exp(E_r/b).$$

With application of an electrolyzing current, I_x, equation [4] becomes

$$[6] \qquad dE/dt = (I_a + I_x)/C - K.\exp(E/b).$$

The initial slope of the build-up curve is given by equation [6] with equation [5] valid at $t = 0$:

$$[7] \qquad (dE/dt)_{t=0} = (I_a + I_x)/C - K.\exp(E_r/b) = I_x/C.$$

For noble metals the value of E_r is small and the exponential term remains small over a considerable portion of the build-up. With aluminum the condition is quite different. The rest potential represented from 50 to 85% of the ultimate overpotential in the range of conditions used here. Therefore the exponential term was appreciable at all stages of the build-up and not even the initial part of the build-up curve was linear. The initial slope was determined by extrapolation to zero time of the secants from the rest potential to the first several points on the build-up curve. Table II gives the data for cathode III, for example.

TABLE II

C FROM SLOPES OF BUILD-UP CURVES

i_x, μa.cm.$^{-2}$	55	91	127	215	273	364	545	727
C, μf.cm.$^{-2}$	28	25	26	26	22	22	24	17

Potential decay curves also showed complication not found with noble metal. The curves were not superimposable by a simple time shift, θ, as found for silver (4), but a value of Δt could be found such that E was linear in $\log(t + \Delta t)$ over the first 90% of the decay curve. With the assumption that Δt corresponds to θ, C was calculated as $(I_a + I_x).\Delta t/k$; the value of k was determined from the slope of the curve of E against $\ln(t + \Delta t)$. Values of C were also calculated by a method similar to that used for the build-up curves. After a build-up of potential there exists a steady state of overpotential and a steady state of cathodic current. Equation [4] then takes the form

$$[8] \qquad 0 = dE/dt = (I_a + I_x)/C - K.\exp(\eta/b).$$

When the electrolyzing current is removed, $I_x = 0$ and equation [4] takes the form appropriate to decay

$$[9] \qquad (dE/dt)_{t=0} = I_a/C - K.\exp(\eta/b) = -I_x/C.$$

Table III shows values of C calculated by the two methods, for sample III.

TABLE III

QUANTITIES DETERMINED FROM DECAY MEASUREMENTS

i_x, μa.cm.$^{-2}$	91	127	215	364	727
$-dE/d[\log(t+\Delta t)] = k$	0.195	0.262	0.257	0.204	0.194
C, μf.cm.$^{-2}$, eq. [9]	22	17	24	20	20
$C = (i_a+i_x).\Delta t/k$	32	32	31	19	16

ACKNOWLEDGMENTS

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SKELETAL SILVER CATALYSTS FOR THE OXIDATION OF ETHYLENE TO ETHYLENE OXIDE[1]

By A. Cambron[2] and W. A. Alexander

ABSTRACT

Skeletal silver catalysts of high specific activity have been prepared by the removal of calcium from calcium–silver alloys. The activity of these catalysts in the oxidation of ethylene to ethylene oxide has been investigated. Catalysts prepared by the removal of the other alkaline earth metals from their alloys with silver have also been studied. It has been found that catalysts prepared from calcium–silver alloys show a higher specific activity and are more stable and more conveniently prepared than the catalysts from the other silver alloys investigated.

INTRODUCTION

The increasing interest in ethylene oxide as a starting material in organic syntheses is shown by the numerous references in the recent current and patent literature not only to improved methods of producing this versatile chemical, but also to its use in the preparation of other aliphatic chemicals and derivatives. A survey of the literature was included in a recent communication (7).

Considerably more work has been done on the direct oxidation of ethylene to ethylene oxide than on the older chlorohydrin method since the specific activity of silver as a catalyst in that reaction was first reported by Francon (4). The reason for this is that the direct catalytic oxidation offers a more attractive method provided the complete oxidation of ethylene, which is also promoted by the silver catalyst, is limited.

Metallic silver is the only substance which has been found to have a specific catalytic effect on the oxidation of ethylene to ethylene oxide. The methods described in the literature for the preparation of silver catalysts have been almost exclusively by the precipitation of the finely divided metal or of the oxide, from solutions of a silver salt or by the thermal decomposition of a silver salt. The use of numerous oxides or metals as promoters has also been mentioned in the literature (8, 11, 13), but in all cases the oxides are added as a distinct solid phase, or the added metal remains in the catalyst.

The preparation of an active catalyst by the thermal decomposition of silver oxalate in the presence of water under pressure was described in a previous paper (7). It was found that the activity of the latter catalyst could be increased by the use of lime and stannous oxide as promoters. The pronounced action of calcium oxide as a promoter even when present in very small amounts suggested that a reduction of the calcium oxide by silver might take place locally on the surface of the catalyst, resulting in alteration in the surface of the catalyst by the momentary formation of a calcium silver compound, followed by the regeneration of calcium oxide and of metallic silver by the action of the oxygen in the reacting gases. Dowden (3) in a recent paper has

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[2]*Deceased February, 1952.*

pointed out the possibility that irreducible oxides in the presence of a reducing metal such as copper, and one would expect silver to behave similarly, may lead to the formation of a metallic surface phase. Even if this only resulted in the formation of a chemisorbed layer of the added metal, it would be expected to have a strong influence on the activity of the surface.

In the previous work on the use of calcium oxide as a silver catalyst promoter, it was observed that this oxide, in addition to promoting the oxidation of ethylene to ethylene oxide, also strongly promoted the complete oxidation of ethylene to carbon dioxide and water. In order to study the effect of calcium on the catalyst surface in the absence of calcium oxide a calcium–silver alloy was prepared and the activity of the surface was determined after removing the calcium metal with a suitable reagent. In this manner a very active and very stable skeletal silver catalyst was obtained which possessed an appreciably higher selectivity than finely divided silver catalysts prepared by known methods.

EXPERIMENTAL

In order to determine the effect of the removal of the calcium component of the alloy on the structure of the remaining silver skeleton, an X-ray examination of the alloy was made. This gave a spectrum different from that of silver owing to the presence of the calcium–silver compound and of a eutectic. After removal of the calcium the characteristic silver lines corresponding to the face-centered cubic arrangement of crystalline silver reappear and the sharpness of these lines indicates that the silver crystal units must form particles of the order of 1000 Å in size.

The first calcium–silver alloys were prepared with a calcium content of 5–7%. It was found, however, that complete removal of the calcium required prolonged treatment of the alloy with steam after grinding to 20–30 mesh. Alloys were therefore prepared with a higher calcium content, in the range 7–12% calcium. These are considerably more brittle and could be ground conveniently to the required size for complete removal of the calcium. It is interesting to note that the calcium–silver alloys themselves possess no specific activity in the oxidation of ethylene and that maximum specific activity is obtained by as complete a removal as possible of the calcium.

In the course of the work done on the preparation of skeletal silver catalysts from silver alloys a number of other alloying elements from groups one to four have been studied, namely lithium, magnesium, strontium, barium, zinc, aluminum, lanthanum, cerium, and tin. Although a few of these alloys showed some activity after complete or partial removal of the alloying elements, with the possible exception of barium none showed as high a specific activity as the catalysts prepared from calcium–silver alloys. This may in part be due to the fact that the removal of calcium from the calcium–silver alloy can be done more readily and under less drastic conditions than is the case with the other metals.

Preparation of Silver–Calcium Alloys

The calcium–silver alloys were prepared by melting the required amount of silver in a crucible made from a stainless steel or iron tube, fitted with a

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$\frac{1}{4}$ in. iron thermocouple tube which also served as a hand stirrer and was so arranged that an argon atmosphere would be maintained in the crucible. A slight excess of freshly cleaned calcium metal was then added to the molten silver. After the molten mass was kept above the melting point of the alloy for about one minute with stirring, the alloy was allowed to cool, or was quenched, and the solid ingot obtained was recovered by stripping off the metal tube. By a later procedure, especially with large melts, the silver was first allowed to solidify and then dissolved slowly by alloying with the calcium at 750° to 850°C., to decrease the rate of gas evolution and to eliminate the danger of a mild explosion.

Silver alloys of other alkali and alkaline earth metals were prepared by the same procedure.

Activation of Silver Catalysts

Several methods were tried for removing the added metal from the silver alloys. Simple refluxing in acetic acid with or without diluted oxidizing agents such as hydrogen peroxide or potassium permanganate did not produce a highly active catalyst. Since the present work was concerned mainly with alloys of silver with metals of groups II and III, many of which react with steam at temperatures below 350°C., the usual initial step in the activation procedure was the treatment of the alloys, ground to about 20–30 mesh, with steam at 300–450°C. for about six to eight hours, or with water in an autoclave at 200–250°C. for about four hours. Control of temperature in the activation treatments is necessary and is aided by use of only small amounts of powder in one place to prevent accumulation of heat of reaction. With silver alloys containing magnesium, strontium, and barium, it was found difficult if not impossible to react the added element completely. Tests carried out with other than calcium alloys were therefore qualitative in character, but did indicate that the calcium alloy was the most convenient to use.

Variations in the activation procedure which were successful included the heating of the alloy in a moist air stream or in the off-gas from a reactor for long periods at about 400°C. followed by leaching with warm acetic acid. Refluxing in acetic acid with repeated additions of 5% hydrogen peroxide, treatment with 15% nitric acid, and variations of the autoclaving such as addition of alcohol, hydrogen peroxide, dioxane, phenol, borax, and ethylene glycol to the water resulted in only normally active catalysts.

After conversion of the added element to the hydroxide by steam, the latter was leached out by refluxing with 20% acetic acid for one hour followed by washing the residue with distilled water and sometimes alcohol. Formic and citric acids may also be used to dissolve the calcium hydroxide.

Apparatus and Materials

The test apparatus arrangement was similar to that described before (7) except that the ethylene was taken directly from the cylinder and the reaction tubes now consisted of $\frac{1}{2}$ in. diameter holes in an aluminum block. The bottom of each reaction hole was closed by a bed of coarse silver granules which served as a preheater for the reactants. Most alloys were crushed to 20–35 mesh,

and weighed lots placed on top. The temperature was measured by a chromel alumel thermocouple with a silver strip about $\frac{1}{4}$ in. $\times$ 1 in. $\times$ 0.020 in. brazed to the junction, which was covered by the catalyst. The products were normally vented to a water tower and the solution discarded, or passed to the analytical part of the apparatus. No change was made in the analytical procedures.

Ethylene of U.S.P. grade was obtained from the Ohio Chemical Co. and produced by the dehydration of alcohol. It was used without further purification. The air supply was passed through an activated charcoal bed and, in later tests, through a tube containing heated silver catalyst as well. Both reactant streams were measured by calibrated flowmeters. The silver was mint grade granules and the calcium, magnesium, strontium, and barium probably distilled products of the Dominion Magnesium Company.

Some attempts were made to modify the disposition of the catalyst bed, for better temperature control on a larger scale. Pressing of the silver granules into pellets using various pressures showed that the activated catalyst could not be deformed without loss of activity. However, further tests with alloys having some plasticity showed that active catalysts could be prepared from pellets or disks of alloy granules. Mixing the alloy granules with other metal powders to improve the bonding showed that aluminum, brass, iron, and monel decreased the activity severely, while pure silver was neutral.

RESULTS

As mentioned above, calcium–silver alloys produced the most stable catalysts with the highest activity. Usually catalysts from these alloys exhibited an increase in activity, as measured by selectivity, to a maximum at about 10–20 days with a subsequent slow decrease. This decline was normally very

TABLE I

STABILITY OF CALCIUM–SILVER CATALYST

Composition: initial: Ca 9.25%, Ag balance; activated: Ca 0.6%, Ag balance; ethylene: 2.0 l./hr.; air 30 l./hr.; catalyst weight: 17 gm.; mesh: −20+35; volume: 7.9 cc.

	Temperature		Conversion %'s		
Day	Catalyst	Block	C_2H_4O	Total	Selectivity
1	285	259	39.3	96.0	41.0
9	277	259	42.0	81.5	51.5
33	270	260	41.5	76.0	55.0
43	287	275	45.0	87.5	51.5
71	260	260	35.3	66.1	53.5
111	266	261	40.6	75.0	54.1
149	272	263	39.6	81.7	48.5
195	262	260	18.7	27.6	67.8
201	266	261	42.3	74.0	57.2
232	286	278	46.6	88.8	51.4
261	266	264	21.8	37.0	57.0
291	269	263	40.3	75.1	53.7
327	266	260	35.3	72.1	49.1
344	263	260	35.1	68.1	51.4
350	—	260	15.2	23.0	66.1
365	263	260	32.3	60.5	53.4

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slow as numerous tests were carried on for periods of up to about 12 months, with a high level of activity at the end of the test. One such experiment is summarized in Table I. This catalyst was activated by treating with steam for one-half hour, at 150°C. initially and gradually raising the temperature to 350°C., followed by one hour at 340–355°C. The lime was removed by 20% acetic acid followed by water and methanol washings. This test was carried on for more than a year, the catalyst being poisoned by unknown substances three times with subsequent recovery to normal activity levels. Results with a number of calcium–silver alloy catalysts are shown in Table II. Activation of

TABLE II

ACTIVITIES OF CATALYSTS FROM CALCIUM–SILVER ALLOYS
Ethylene: 2 l./hr.; air: 30 l./hr.; block temperature: 260°C.

Composition, %Ca			Duration of test,	Catalyst tempera-	Typical conversion %'s			Catalyst	
Initial	Final	Day	days	ture, °C.	C_2H_4O	Total	Selectivity	Wt., gm.	Mesh
9.5	1.25	37	78	263	42	66	64	20	20–35
10.3	4.3	10	37	268	36	67	53	16	20–35
9.9	1.4	26	37	272	46	87	53	16	20–35
8.2	0.3	27	60	274	43	83	52	16	20–35
6.5	1.8	9	25	270	32	64	51	16	20–35
9.6	0.2	44	161	274	46	76	60	16	10–20
10.3	0.0	60	111	272	47	86	55	16	20–35

these alloys was by heating in a current of steam at 300° to 400°C., followed by leaching with acetic acid and with water. As complete removal of calcium as possible from an 8 to 11% alloy is the preferred procedure, since a high residual calcium content apparently decreases the stability of the catalyst.

Catalysts prepared from magnesium and strontium alloys showed a lower selectivity at comparable total reaction levels than calcium–silver. Barium apparently approached the activity of calcium, but for economic reasons and because of its reactivity it was not extensively tested. Results obtained with these alloys are shown in Table III, from which it will be noted that the yields are considerably lower than with the calcium alloys of Table II.

TABLE III

ACTIVITIES OF SILVER CATALYSTS FROM MAGNESIUM, STRONTIUM, AND BARIUM ALLOYS
Ethylene: 2 l./hr.; air: 30 l./hr.

Composition, %		Temperatures, °C.		Typical conversions, %			Gm. of catalyst	
Initial	Final	Block	Catalyst	C_2H_4O	Total	Selectivity		Activation procedure
Mg 53	6.4	213	375	16	82	19	11.5	Steam at 375°, leach with acetic acid
Mg 17	13	260	264	12	28	43	16	Steam at 375°, leach with acetic acid
Sr 5	—	200	222	12	32	39	—	Moist air at 400° for 45 hr., leach with acetic acid
Ba 5	—	270	273	4	11	35	—	Moist air at 400° for 45 hr., leach with acetic acid
Ba 21	3	259	264	35	91	38	16	Steam at 375°C., leach with acetic acid
Ba (3)	0.2	249	276	37	85	43	15.6	Reactivated above catalyst by above procedure

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TABLE IV

ACTIVITIES OF CATALYSTS FROM CALCIUM–MAGNESIUM–SILVER ALLOYS
Ethylene: 2 l./hr.; air: 30 l./hr.; catalyst size: −20+35 mesh

Composition, %		Temperatures, °C.		Typical conversion, %				
Initial	Final	Block	Catalyst	C_2H_4O	Total	Selectivity	Day	Gm. of catalyst
Mg 19.8 Ca 4.3	10.7 0.0	250	278	26	83	31	16	16
Mg 10.3 Ca 4.8	0.0 0.0	259	273	27	94	28	9	16
Mg 5.4 Ca 5.8	0.0 0.2	265	274	16	48	34	2	15.3
Mg 5.0 Ca 9.3	0.0 0.2	260	272	46	98	47	13	16
Mg 2.5 Ca 11.6	0.0 0.4	259	271	43	98	44	11	16

Experiments with the ternary magnesium–calcium–silver alloys are summarized in Table IV. These were activated by steaming at 350° to 375°C. and leaching with acetic acid followed by washing with water and drying. As mentioned earlier, the removal of a large excess of magnesium is difficult, and the yields or selectivities of the resulting catalysts tend to be considerably lower than with calcium–silver alloys. Catalysts prepared from alloys with an excess of calcium apparently show activities similar to the binary calcium–silver alloys.

Several metals from groups I to IV of the periodic table were tried as substitutes for calcium. In some cases the added element could not be removed readily while in others the residual silver showed no enhanced catalytic effect. The possible exceptions are tin and lanthanum, which were, however, inferior to the alkaline earth metals. Other elements tested were sodium, lithium, mercury, and aluminum.

The effects of many promoters, of preconditioning procedures, and of anticatalysts were also investigated. As promoters, many metals were added in minor amounts, some being partially removed during the activation procedure. In no case was any reproducible increase in yield of ethylene oxide observed. The metals tested were copper, manganese, platinum, nickel, zinc, cadmium, mercury, tin, cerium, lanthanum, as well as calcium oxide and calcium carbonate.

As will be noted in Table I the selectivity of the catalyst is usually low for the first 10 to 20 days. This induction period may be reduced to as little as two to three days by heating at the reaction temperature for about one week in an atmosphere of carbon dioxide, oxygen, steam, air, ethylene, and probably other gases. The catalyst then shows normal reactivity in other respects.

The efficiency of halogen compounds (1, 2, 5, 6, 14) and halides (12, 19) as anticatalysts in the suppression of the reaction to carbon dioxide and water has been mentioned frequently in the literature. The use of organic halogen

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compounds has also been suggested in the reactivation of a poisoned catalyst or in the regeneration of an old one with low activity (20). McKim and Cambron (7) found no anticatalytic activity with an organic halogen, but a definite poisoning. The effect of inorganic halide solutions was investigated in the course of the present experiments. In only three instances were moderate increases in activity observed which might be attributed to the sodium chloride and to the hydrogen chloride treatments, the latter apparently being the more effective. Large amounts of halides acted as poisons. There was, however, some indication that this treatment would decrease the induction period in the same way as preheating. The halides tested were hydrogen chloride, potassium chloride, sodium chloride, sodium fluoride, magnesium chloride, and magnesium fluoride. Silver chromate in large amounts also acted as a poison.

On adding ethane to the feed gas, a decrease in selectivity was again observed (7). In seven experiments, 10% ethane was mixed with the ethylene and in only one was an increase in yield observed, amounting to only about 3%. In the remainder decreases of up to about 15% occurred. An additional test with 5% ethane showed a decrease of about 20%. The presence of ethane in these amounts might thus be considered undesirable.

Several papers (9, 10, 15, 16, 17, 18) have discussed the kinetics and reaction mechanisms and nothing can be added from this work. Various engineering developments in the use of these catalysts have been made in these laboratories, such as the means of disposal of the catalyst in the reactant stream to maintain close temperature control and achieve optimum reactivity. These will undoubtedly be discussed in future publications.

ACKNOWLEDGMENT

The assistance of many members of the staff of the National Research Council who contributed directly or indirectly to this work while in progress is gratefully acknowledged. Thanks are also due to Dr. I. E. Puddington for reading the manuscript.

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THE SYSTEM LiCl–NaCl–KCl–H_2O AT 25° C.[1]

By A. N. Campbell and E. M. Kartzmark

ABSTRACT

Of the component ternary systems of the quaternary system LiCl–NaCl–KCl–H_2O, the system LiCl–KCl–H_2O has not previously been investigated. This has now been done and it is shown to be very similar to the system LiCl–NaCl–H_2O investigated by Smits, Elgersma, and Hardenberg (4). In both systems, the strongly hydrated lithium ion reduces the content of second salt to a low value at the (isothermal) invariant point.

The quaternary system of the title has been investigated, using a new method of analysis which involves the determination of total chloride and of density. The quaternary invariant composition is similar to that of the ternary invariant in the system LiCl–KCl–H_2O. In none of these systems is there formation of double salt or solid solutions and the only hydrate occurring as a solid phase is LiCl.H_2O.

The study of this system was undertaken as the first part of a comprehensive study of the five-component system containing the radicals Li_2, Na_2, K_2, Cl_2, and SO_4, and water. A similar comprehensive study on the ions of sea-water was made by van't Hoff (5) but his investigation did not extend to lithium. The present study includes, in addition to the system now described, the ternary systems (1) Li_2Cl_2–Li_2SO_4–H_2O, (2) Na_2Cl_2–Na_2SO_4–H_2O, (3) K_2Cl_2–K_2SO_4–H_2O; the quaternary system Li_2SO_4–Na_2SO_4–K_2SO_4–H_2O; and the reciprocal salt pairs (1) $Li_2Cl_2 + Na_2SO_4 = Na_2Cl_2 + Li_2SO_4$, (2) $Na_2Cl_2 + K_2SO_4 = K_2Cl_2 + Na_2SO_4$, (3) $Li_2Cl_2 + K_2SO_4 = K_2Cl_2 + Li_2SO_4$; as well as the quinquenary system mentioned above. Much of the experimental work involved has already been done but not all of it. The method of graphical representation chosen was that of Jänecke (3), the only one of reasonable simplicity. The axes of representation for Jänecke's system are the edges of a regular equal-sided triangular prism. On this model, the six vertices represent single salts and water, the edges ternary systems, the triangular surfaces quaternary systems, the rectangular surfaces reciprocal salt pairs, and the interior of the model the quinquenary system.

On reviewing the literature of the present study, we found that of the component ternary systems, viz. (1) LiCl–NaCl–H_2O, (2) LiCl–KCl–H_2O, and (3) NaCl–KCl–H_2O, system (3) was well known, and system (1) had been done by Smits, Elgersma, and Hardenberg (4); system (2) was unknown. In view of our own results for system (2) we see no reason to doubt the results of Smits, Elgersma, and Hardenberg for the analogous system (1); it appears that the highly hydrated lithium ion acts very powerfully in displacing other salts from solution, so that the isothermal invariants: LiCl.H_2O, NaCl, solution and LiCl.H_2O, KCl, solution, respectively, contain in solution very little salt other than lithium chloride. Our first task then was to carry out an investigation of the system LiCl–KCl–H_2O, at 25° C., preparatory to a study of the quaternary system named in the title.

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Contribution from the Chemistry Department, University of Manitoba, Winnipeg, Manitoba.

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EXPERIMENTAL

The technique of preparing and filtering saturated solutions is too well known to merit description. For the investigation of the ternary system we used Schreinmakers' method of the 'wet rest'. No such method is available for the quaternary system, neither is it necessary since the nature of all solid phases is known. The chemicals used were all either B.D.H. 'Analar' or Merck's 'reagent' grade. They were used without further purification since very slight traces of impurity are without effect on studies of this kind.

The great difficulty in studies involving mixtures of alkali cations is a method of analysis. Any chemical method would be laborious and too inaccurate for the present purpose. It is possible in theory, however, to analyze any three-component mixture by determining any two physical properties for all proportions of the three components. One of us used the method, very successfully, for the analysis of liquid mixtures of benzene – ethyl alcohol – carbon tetrachloride (2), but here the problem is simpler, since the amount of water does not enter as a fourth variable. To overcome this difficulty we proceeded in the following way: after determining total solubility in the usual manner, exactly 10 gm. of the anhydrous solid mixture was dissolved in water and diluted to exactly 100 ml. and the density and total chloride content determined. Because of the very hygroscopic nature of lithium chloride, it was not advisable to weigh exactly 10 gm. of the mixture and therefore the total weight of solid mixture was dissolved in water, the solution weighed, such an aliquot taken as corresponded to 10 gm., and this then made up to 100 ml. In their study of the system LiCl–NaCl–H_2O, Smits, Elgersma, and Hardenberg (4) used the viscosity of mixtures of constant total composition as the analytical method. When the chloride contents and densities, or rather the density minus one, of all possible mixtures of LiCl, NaCl, and KCl, are plotted on two separate triangular diagrams, and points of equal density and of equal chloride content respectively are joined by curves, the method of analysis is complete. The density of an unknown mixture places it on a curve of density and its chloride content on a curve of chloride content. Since fortunately these two curves always intersect sharply, the point of intersection represents the composition of the mixture. On previous occasions, we had adopted the method of placing one diagram exactly above the other and illuminating strongly from below. In the present instance, we found it better to plot both sets of results on one diagram, as shown in Fig. 1.

The densities were determined in a 25 ml. specific-gravity bottle. In order to obtain an accuracy of one per cent in the analysis, the density must be determined to two units in the fourth decimal place. Since we were able to obtain a reproducibility of one in the fourth decimal place, we feel we attained an analytical accuracy of $\pm 1.0\%$, as far as the density determinations are concerned. Since, however, the analysis of a ternary mixture depends also on the chloride determination, we feel that the over-all accuracy is somewhat less than this, but it is much better than any chemical method.

In preparing the calibration curves, the chloride content was simply calculated from the formulae of the chlorides, for all possible mixtures. In de-

termining the chloride content of unknowns, we titrated conductimetrically with silver nitrate. In the analysis of the simple ternary system LiCl–KCl–H_2O, it was of course unnecessary to determine both chloride content and density, and we used chloride content alone for this purpose.

EXPERIMENTAL RESULTS

Table I contains our density determinations, which were used in the calibration; the chloride content is also included. When plotted against composition, either as binary or ternary mixture, the density curves are straight lines, as are those of chloride content.

TABLE I

DENSITIES AND CHLORIDE CONTENT OF MIXTURES OF LiCl, NaCl, AND KCl OF TOTAL WEIGHT 10 GM. IN 100 ML. OF SOLUTION, AT 25.0° C.

% LiCl	% NaCl	% KCl	$d_4^{25^\circ}$	% Cl
100	—	—	1.0519	83.62
80	20	—	1.0543	79.03
60	40	—	1.0568	74.43
50	50	—	1.0583	72.14
40	60	—	1.0594	69.85
20	80	—	1.0618	65.25
—	100	—	1.0644	60.66
—	80	20	1.0630	58.04
—	50	50	1.0612	54.11
—	20	80	1.0592	50.18
—	—	100	1.0579	47.56
20	—	80	1.0568	54.77
50	—	50	1.0550	65.59
80	—	20	1.0532	76.41
80	10	10	1.0537	77.73
50	20	30	1.0562	68.21
30	50	20	1.0594	64.93

Table II contains the results for the system LiCl–KCl–H_2O at 25° C. The equilibrium diagram is given as Fig. 2.

TABLE II

COMPOSITION OF SATURATED SOLUTIONS AND NATURE OF SOLID PHASES IN THE SYSTEM LiCl–KCl–H_2O AT 25° C.

Composition				Nature of solid phase
Liquid phase		'Wet' solid phase		
Wt. % LiCl	Wt. % KCl	Wt. % LiCl	Wt. % KCl	
45.4	0.0	—	—	$LiCl.H_2O$
44.2	2.3	59.05	0.9	$LiCl.H_2O$
44.7	3.4	56.5	6.3	$LiCl.H_2O$ + KCl
0.0	26.99	—	—	KCl
4.1	21.2	1.2	82.0	KCl
18.5	7.3	3.9	82.7	KCl
23.1	4.7	6.0	78.0	KCl
28.3	3.5	7.8	73.8	KCl
37.8	0.6	10.3	72.4	KCl
45.8	2.9	44.0	9.0	KCl + $LiCl.H_2O$

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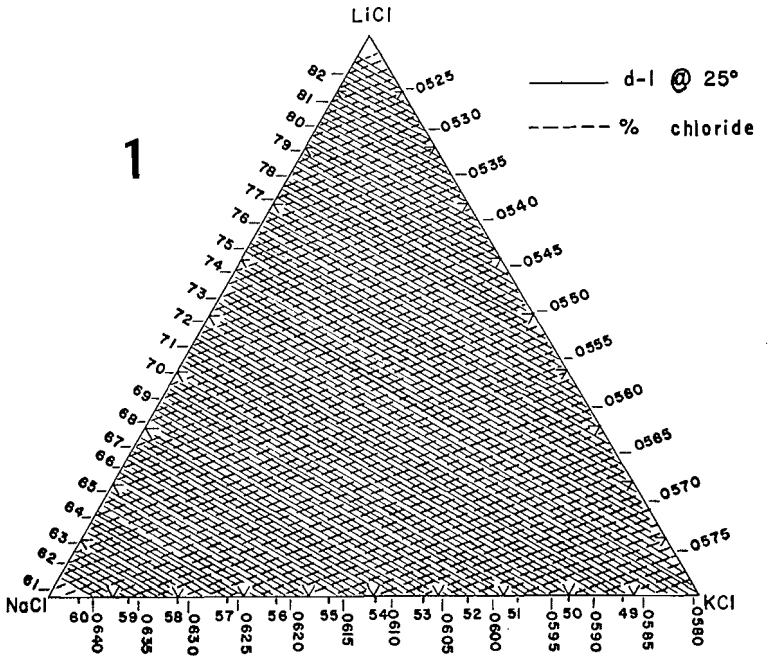

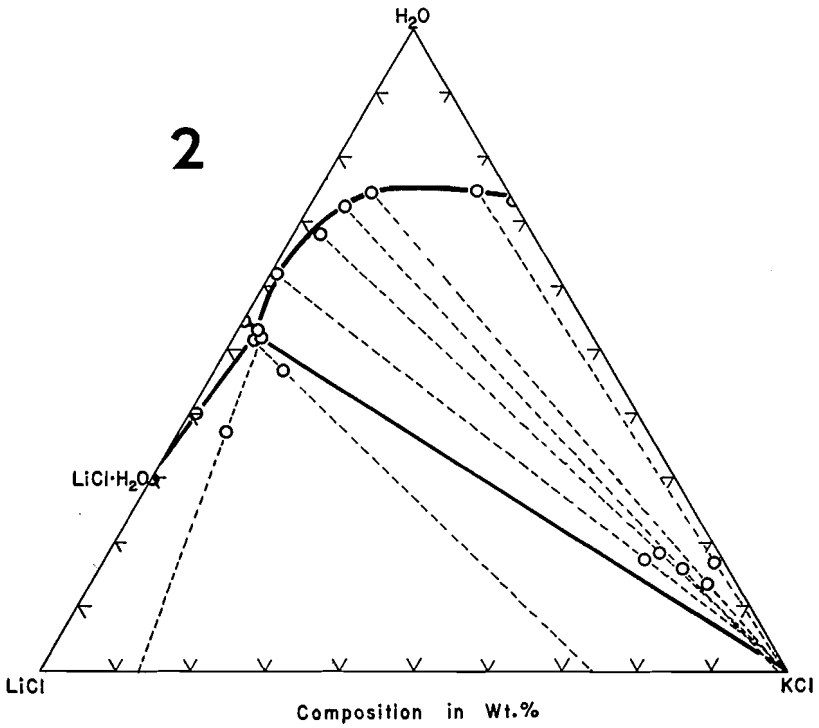

FIG. 1. Density and per cent chloride curves for the analytical method.
FIG. 2. The system LiCl–KCl–H_2O at 25°C.

In order to investigate the quaternary system, LiCl–NaCl–KCl–H_2O, we started with the only ternary isothermal invariant which contains appreciable quantities of two salts, viz. the invariant: KCl, NaCl, saturated solution, and, while keeping potassium chloride and sodium chloride present in excess, we added increasing quantities of lithium chloride, established equilibrium at 25°, and analyzed both liquid and solid phases. The system is of such a simple kind, as we knew from the component ternary systems, that only one quaternary (isothermal) invariant was to be expected, viz. LiCl.H_2O, KCl, NaCl, saturated solution. Moreover, since the ternary invariants with LiCl.H_2O as one solid phase contained very little potassium chloride or sodium chloride respectively in solution, we expected that the quaternary invariant would likewise contain little other than lithium chloride in solution. The point of analyzing the solid phase was that, so long as LiCl.H_2O was not a solid phase, the lithium chloride content of the solid phase would be entirely due to adhering mother liquor but, as soon as LiCl.H_2O appeared as a solid phase, the lithium chloride content would increase sharply. Our results are contained in Table III.

TABLE III

COMPOSITION OF EQUILIBRIUM SOLUTIONS AND OF SOLID PHASES IN THE SYSTEM LiCl–NaCl–KCl–H_2O

Composition						Nature of solid phase
Liquid phase			'Wet' solid phase			
% LiCl	% KCl	% NaCl	% LiCl	% KCl	% NaCl	
—	10.4	21.1	—	27.0	56.7	KCl + NaCl
8.2	7.6	10.7	0.8	17.9	62.5	KCl + NaCl
8.1	8.8	12.5	2.0	13.8	63.3	KCl + NaCl
32.9	1.3	2.2	7.3	29.5	43.2	KCl + NaCl
4.5	9.9	15.7	Trace	40.6	43.1	KCl + NaCl
41.5	3.1	0.2	34.05	12.2	20.8	KCl + NaCl + LiCl.H_2O

In Table IV the results are calculated in accordance with Jänecke's system of notation, viz.: $m$$H_2O$, aLiCl, bKCl, $(1-a-b)$NaCl, where a, b, and $(1-a-b)$ are the mole fractions of LiCl, KCl, and NaCl respectively, and m is the number of moles of water to one total mole of salt in solution.

TABLE IV

THE SYSTEM LiCl–NaCl–KCl–H_2O AT 25° C., CALCULATED BY THE JÄNECKE SYSTEM OF NOTATION

a	b	m	Nature of solid phase
0.00	0.388	7.60	NaCl + KCl
0.405	0.212	8.52	NaCl + KCl
0.649	0.402	7.49	NaCl + KCl
0.935	0.021	4.25	NaCl + KCl
0.210	0.263	7.61	NaCl + KCl
0.955	0.041	2.98	NaCl + LiCl.H_2O + KCl

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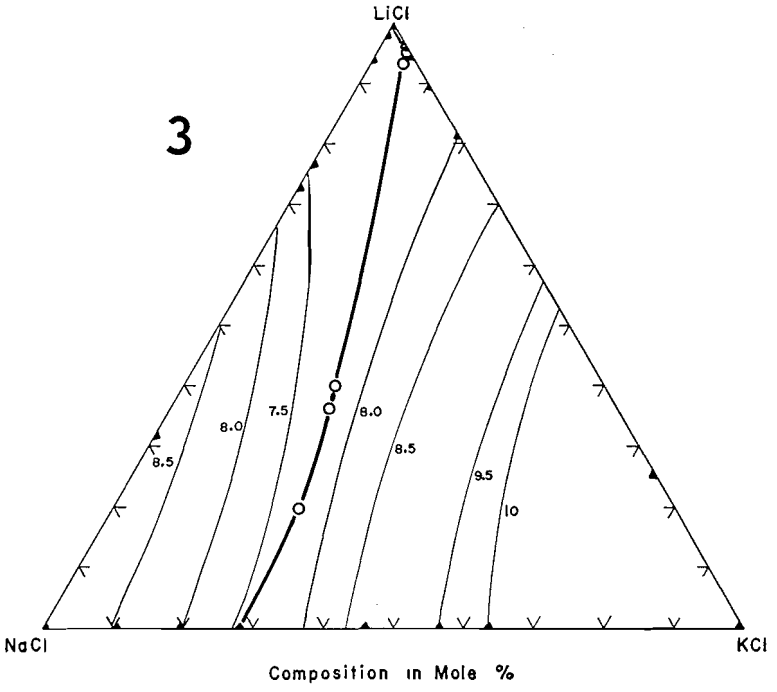

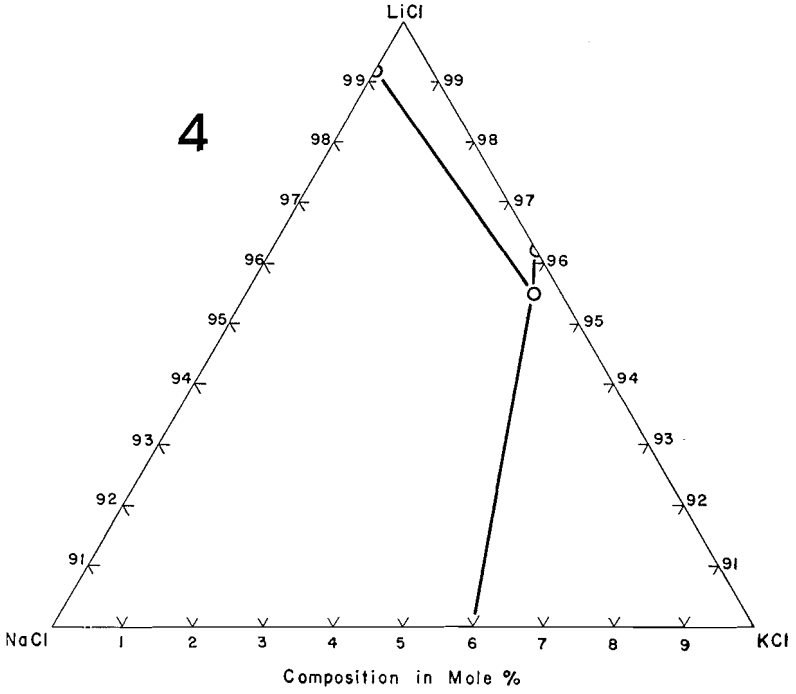

FIG. 3. The system LiCl–NaCl–KCl–H_2O at 25° in Jänecke representation.
FIG. 4. Enlargement of the quaternary invariant area.

The equilibrium diagram is given as Fig. 3, while Fig. 4 gives an enlarged picture of the lithium chloride corner of the diagram, showing two ternary invariants and the quaternary invariant. In Fig. 3, the isohydrores (lines of equal water content) are drawn in as faint lines.

DISCUSSION

No great discussion is called for, since neither double salts nor solid solutions form, but one or two points of interest emerge. First, the tremendous salting-out effect of the lithium ion is evident in the new system, LiCl–KCl–H_2O, as it was in the system LiCl–NaCl–H_2O, investigated by Smits, Elgersma, and Hardenberg. In the system containing sodium chloride, however, the sodium chloride content is reduced to 0.5 weight per cent at the invariant point, while the corresponding invariant in the potassium chloride system contains 3.2% potassium chloride. Otherwise, the two systems are very similar; for instance, in both there is a range of solutions which contain less sodium chloride or potassium chloride than the invariant solution. Attention has been drawn elsewhere (1) to the tenacity with which the lithium ion holds its water of hydration.

The composition of the isothermal invariant solution in the quaternary system is very similar to that in the ternary system LiCl–KCl–H_2O. The lithium chloride solid phase is always the monohydrate, $LiCl.H_2O$.

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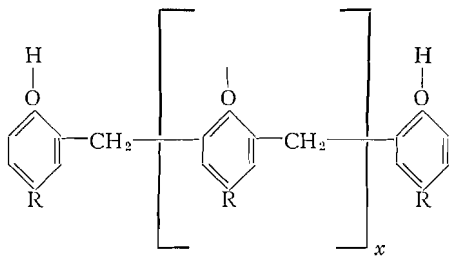
INFLUENCE OF THE NUMBER OF CARBON ATOMS OF THE ALKYL GROUP ON POLYMERIZATION AND PROPERTIES OF PARA-ALKYLPHENOL–FORMALDEHYDE POLYMERS[1]

By A. Rosenthal, F. Lederer, and K. Gilson

ABSTRACT

The polymerization (in organic media) of *p*-cresol–formaldehyde has been investigated in sealed tubes and in open systems. A series of almost colorless *p*-alkylphenol–formaldehyde polymers, prepared in sealed tubes, was studied to determine the influence of the number of carbon atoms of the substituting alkyl group on the polymerization process and on the properties of the polymers. Infrared spectra and chemical analyses of the original and heat-treated polymers were correlated with the structures of the polymers.

Para-alkylphenol–formaldehyde polymers have been little investigated. In 1930 the first completely oil-soluble phenolic resin was reported (3). Turkington and Allen (20) published the first comprehensive review of the properties and general preparation in open systems of oil-soluble phenolic resins, including a rather general evaluation of the varnishes made from these resins. Shreve and Golding (18) attempted to evaluate what they believed to be the best of the phenolic compounds for making varnishes. In work connected with a structural determination of Koresin, Marvel and co-workers (13) prepared and studied a few *p*-alkylphenol–formaldehyde resins. Although there is an extensive patent literature on oil-soluble resins, almost all of the preparative techniques involve the use of open systems and inorganic substances, in aqueous media, as catalysts. Considerable fundamental information on the condensation of formaldehyde with substituted phenols has been obtained from the model studies of Zinke (22, 24), Hultzsch (10), and others (6). Individual members of a polymer homologous series from *p-tert*-butylphenol and formaldehyde (I) were prepared by Zinke and co-workers (23).



I; $x = 0$ to 6

It was the first objective of the work herein reported to prepare, under carefully controlled conditions, a homologous series of *p*-alkylphenol–formaldehyde polymers having structure I (R = alkyl group), and to study in a quanti-

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Contribution from the Department of Chemistry, The University of British Columbia, Vancouver, B.C.

tative way the effect of the aliphatic side chain on the polymerization process. A second objective was to study the structures and properties of these polymers.

The *p*-alkylphenol–formaldehyde polymers were prepared at 130° in sealed Carius tubes using bis-(2-ethoxyethyl) ether as solvent, *s*-trioxane as a source of formaldehyde, and *p*-toluenesulphonic acid monohydrate as catalyst. The crude resins were freed of insoluble material and reprecipitated from water. Almost completely colorless solid resins, which were soluble in N,N-dimethylformamide or pyridine, were obtained. The use of a closed system rather than an open one permitted an excellent control of conditions as evidenced by the fact that agreement in specific viscosities of the resins obtained in repeat runs was ±3%. Polymerization of *p*-cresol with formaldehyde under a closed system led to the production of a resin having approximately twice the specific viscosity of one obtained under similar experimental conditions except for that of carrying out the polymerization under reflux in an open system (Table I, polymers 4 and 14).

TABLE I

PREPARATION OF *p*-CRESOL–FORMALDEHYDE POLYMERS

Polymer No.	Moles[a] CH_2O	Solvent[b] in ml.	Tube length, cm.	Time, hr.	Temp., °C.	% soluble[c]	Specific viscosity[d]
1	1.01	5	40	20	110	100	0.037
2	1.03	5	40	20	110	100	0.040
3	1.01	5	40	20	120	98	0.078
4[e]	1.01	5	40	17	130	80	0.091
5	1.03	5	40	17	130	90	0.103
6	1.00	5	40	20	150	70	0.098
7	1.01	5	40	4	130	100	0.041
8	1.01	5	40	10	130	85	0.071
9	1.01	5	40	20	130	77	0.092
10[f]	1.01	10	40	20	130	72	0.106
11[g]	1.01	15	40	20	130	76	0.110
12[h]	1.01	5	10	20	130	57	0.108
13[i]	1.01	5	20	20	130	80	0.085
14[j]	1.01	5	—	20	130	93	0.049

[a]*Per mole of p-cresol; 0.100 mole of p-cresol was used in each run.*
[b]*Bis-(2-ethoxyethyl) ether was used as solvent.*
[c]*At 80–90° with 4 gm. of crude polymer per 100 ml. of N,N-dimethylformamide.*
[d]*At 25° with 0.5 gm. of soluble portion of polymer per 100 ml. of N,N-dimethylformamide.*
[e]η_{sp} *of duplicate was 0.090.*
[f]η_{sp} *of duplicate was 0.108.*
[g]η_{sp} *of duplicate was 0.109.*
[h]η_{sp} *of duplicate was 0.110.*
[i]η_{sp} *of duplicate was 0.087.*
[j]*Polymerization carried out in a flask fitted with a reflux condenser.*
The softening point of polymer 1 was 230–235°, and those of 3, 4, and 8 were 240–245°.

The effects of varying temperature, reaction time, volume of solvent, and tube length on the polymerization of *p*-cresol–formaldehyde polymers (as revealed by specific viscosities) are shown in Table I. An increase of 1 to 3% molar excess of formaldehyde over *p*-cresol resulted in no significant increase in specific viscosities of the polymers when the condensation was carried out at 110° (polymers 1 and 2). When the polymerization was carried out at 130°, a 2% molar increase in formaldehyde gave approximately a 10% increase in specific viscosity (polymers 4 and 5). Although use of equimolar quantities of

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reactants at a temperature of 150° might be expected to yield a much higher molecular weight polymer than was obtained at 130°, such a result was not attained as seen in polymer 6.

At constant molar ratios of reactants an increase in polymerization temperature from 110° to 130° led to an increase in specific viscosities of the polymers from 0.037 to 0.091 and also a 20% increase in the amounts of insoluble material (Table I, polymers 1 and 4). Previous workers (1, 8, 23) have suggested reasons for the partial insolubility of some *p*-alkylphenol–formaldehyde polymers. Infrared studies did not reveal any significant difference in the structures (as shown by the spectra) of the soluble and insoluble fractions of the *p*-cresol–formaldehyde polymers (Fig. 1, polymer 1 and Fig. 2, 4*d*).

It was surprising to discover that a less soluble phenol–formaldehyde polymer was obtained when the Carius tube length was decreased from 40 to 10 cm. (other conditions being the same), although the specific viscosities of the soluble portions of the polymers were essentially the same (Table I, polymers 11 and 12).

The effect of the *p*-alkyl group on the degree of polymerization of *p*-alkylphenol–formaldehyde polymers is shown in Table II. It is interesting to note

TABLE II

PREPARATION OF *p*-ALKYLPHENOL–FORMALDEHYDE POLYMERS[a] IN SEALED CARIUS TUBES

p-Alkyl groups	Polymer No.	% soluble[b]	Specific viscosity[c]	Softening point, °C.[d]	Theoretical formula	Analytical† Calc. C	Calc. H	Found C	Found H
Methyl	4	80	0.091	240–245	$(C_8H_8O)_x$	80.00	6.71	76.42	7.20
Ethyl*	15	80	0.069	210–215	$(C_9H_{10}O)_x$	80.58	7.51	76.81	7.70
n-Propyl	16	98	0.064	210–215	$(C_{10}H_{12}O)_x$	81.02	8.16	80.01	8.80
Isopropyl	17	98	0.069	245–250		81.02	8.16	78.59	8.28
n-Butyl*	18	96	0.048	205–210	$(C_{11}H_{14}O)_x$	81.41	8.70	80.24	8.67
Isobutyl	19	100	0.067	230–235				80.17	8.49
sec-Butyl	20	90	0.139	205–210				80.07	8.71
tert-Butyl	21	98	0.046	195–200				79.97	8.84
n-Amyl	22	95	0.045	195–200	$(C_{12}H_{16}O)_x$	81.77	9.15	80.52	9.11
Isoamyl	23	100	0.051	225–230				80.52	9.29
sec-Amyl*	24	95	0.112	105–110				80.39	8.98
tert-Amyl	25	100	0.051	165–170				79.89	9.00
n-Hexyl	26	100	0.042	190–195	$(C_{13}H_{18}O)_x$	82.08	9.54	80.84	9.65
tert-Octyl	27	100	0.014	80–85	$(C_{15}H_{22}O)_x$	82.52	10.16	82.26	10.20

[a]*Prepared from 0.100 mole p-alkylphenol, 0.101 mole formaldehyde (s-trioxane), 5 ml. bis-(2-ethoxyethyl) ether, and 0.20 gm. p-toluenesulphonic acid monohydrate. Reaction run at 130° for 20 hr. Tube length was 40 cm.*

[b]*At 80–90° with 4 gm. of crude polymer per 100 ml. of N,N-dimethylformamide.*

[c]*At 25° with 0.5 gm. of purified polymer per 100 ml. of N,N-dimethylformamide.*

[d]*Taken in capillary tubes.*

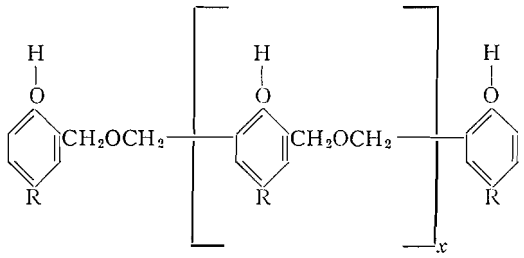
η_{sp} of duplicates of 15, 18, and 24 were 0.067, 0.047, and 0.114, respectively. 4-sec-Amylphenol—$CH_3(CH_2)_2CH(CH_3)C_6H_4OH$.

†*Microanalyses by: Dr. W. Mänser, Nerdstr. 140, Zurich 37, Schweiz.; Drs. G. Weiler and F. B. Strauss, 164, Banbury Road, Oxford, England.*

that as the straight chain alkyl group increased in size from methyl to *n*-hexyl the specific viscosities of the polymers decreased from 0.091 to 0.042 (polymers 4, 16, 18, 22, and 26). Polymers obtained from *p-sec*-butylphenol and *p-sec*-

amylphenol had more than double the specific viscosities of those obtained from the isomeric branched-chain or straight-chain *p*-alkylphenols (polymers 19 to 25). Other workers (18, 14), who have studied the properties of the varnishes from resins of several *p*-alkylphenols, have found that the alkyl group has an effect on the time of resinification.

A surprising and interesting finding was the wider divergence of the experimental per cent carbon from the theoretical of polymers prepared from *p*-cresol than of those prepared from the other *p*-alkylphenols (Table II, Analytical). It might have been expected that the reverse would have been the case, since the *p*-cresol–formaldehyde polymer had a higher specific viscosity than most of the other *p*-alkylphenol polymers. A *p*-cresol–formaldehyde condensate having three benzene nuclei has a carbon content of 79.2% and as a result, the low per cent carbon found can not be fully explained on the basis of a high concentration of low molecular weight fractions. Zinke (22) has proposed that benzyl ether linkages (as shown in II) and methylene bridges are formed at



II

temperatures up to 170°, and above these temperatures formaldehyde is evolved leaving a polymer having structure I. If the structure of the *p*-cresol–formaldehyde polymer is more accurately represented by II than by I, the theoretical per cent carbon would be 72% instead of 80%. The fact that the carbon found was 76.4% indicates that more than half of the linkages which bound the phenolic nuclei were methylene bridges. In an attempt to study this problem further, purified *p*-cresol– and *p-sec*-amylphenol–formaldehyde

TABLE III

EFFECT OF HEAT[a] ON VISCOSITY AND COMPOSITION OF *p*-ALKYLPHENOL–FORMALDEHYDE POLYMERS

p-Alkyl group	Polymer No.	Initial specific viscosity[b]	Specific viscosity[b] after heating	Analytical			
				Before heat treatment		After heat treatment	
				C	H	C	H
Methyl	4	0.091	0.019[c]	76.38	6.71	78.74	6.55
sec-Amyl	24	0.112	0.078[c]	80.39	8.98	80.89	9.06

[a]*Purified and dried polymer heated at 182° for three hours under an atmosphere of dry nitrogen.*
[b]*At 25° with 0.5 gm. of polymer per 100 ml. of N,N-dimethylformamide.*
[c]*Polymers darkened in color on heating.*

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polymers having high specific viscosities were heated at 182° for three hours under an atmosphere of dry nitrogen. The *p*-cresol–formaldehyde polymer evolved formaldehyde. When the latter polymer was heated at about 250° for about one minute, a rapid evolution of bubbles accompanied the change in state of the polymer from solid to liquid. Analytical studies (Table III) of the *p*-cresol–formaldehyde polymer heated at 182° showed that the carbon content of the polymer had increased by 2.4% and the hydrogen content remained about the same. There was a decrease in the specific viscosities of the polymers from 0.091 to 0.019. The *p-sec*-amylphenol polymer when heated under the same conditions had approximately the same carbon content and a 30% decrease in specific viscosity (Table III). Infrared studies showed that the band at 1095 cm.$^{-1}$, present in the spectra of both original polymers, was not present in those of the corresponding heat-treated polymers (Fig. 1, polymers 4 to 4*c* and Figs. 4 and 5, polymers 24 to 24*c*). Evidence that the band at 1095 cm.$^{-1}$ is characteristic of a benzyl ether linkage is provided by the fact that the spectrum of dibenzyl ether has a band at 1095 cm.$^{-1}$ whereas that of 4,4′-dihydroxydiphenylmethane does not (16). Zinke (23) and Hultzsch (10) have suggested that the fission of the ether bridge results in the production of phenol aldehydes together with *o*-quinone methides. The presence of the latter degradation products would account for the fact that the polymers darkened after

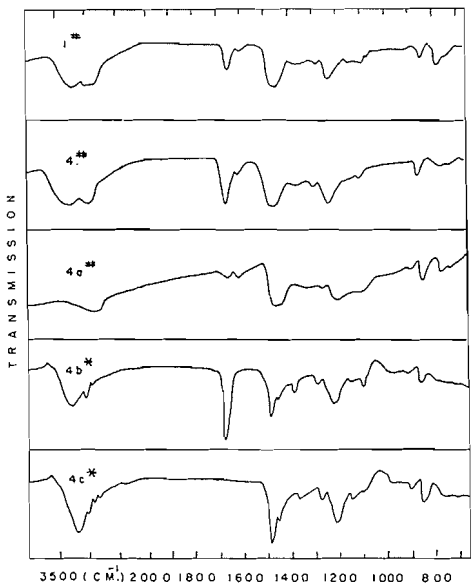

FIG. 1. Infrared spectra of *p*-cresol–formaldehyde polymers:
1‡ *p*-Cresol–formaldehyde (η_{sp} = 0.037).
4‡ *p*-Cresol–formaldehyde (η_{sp} = 0.091).
4*a*‡ *p*-Cresol–formaldehyde (heat-treated; η_{sp} = 0.019).
4*b** *p*-Cresol–formaldehyde (η_{sp} = 0.091).
4*c** *p*-Cresol–formaldehyde (heat-treated; η_{sp} = 0.019).

‡*Nujol mull; other spectra: 5% solution in chloroform.*
**Partially soluble. Insoluble part filtered off.*

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prolonged heating at 182°. Present studies do not permit a correlation of polymer structure with the band at 1670 cm.$^{-1}$ which was present in the spectrum of the original polymer but absent in that of the heat-treated *p*-cresol–formaldehyde polymer.

The softening points of the *p*-cresol–formaldehyde polymers were essentially the same for polymers having specific viscosities ranging from 0.057 to 0.091. A slightly lower value (230–235°) was obtained with a *p*-cresol polymer having a specific viscosity of 0.037 (Table I). The fact that the melting points were found to be essentially independent of the molecular weights of these polymers lends support to the assumption that the polymers being dealt with were of high molecular weight (4). Attempts to obtain molecular weights of the polymers by the Rast method or by the use of benzil as solvent were unsuccessful.

The effect of the alkyl groups upon the softening points of linear phenoplasts is strikingly brought out by the fact that the softening point of *p-sec*-amylphenol–formaldehyde polymer ($\eta_{sp} = 0.112$) was 105–110°, whereas that of the *p*-cresol–formaldehyde polymer ($\eta_{sp} = 0.091$) was 240–245° (Table II, polymers 4 and 24). In this connection it is interesting to note that other workers (4, 9) have recently found that the size and flexibility of alkyl groups have a marked effect on the melting points of linear polyesters. For polymers of approximately the same molecular weight (Table II, polymers 21 and 25), an increase in the size and bulkiness of the alkyl group from *tert*-butyl to *tert*-amyl resulted in approximately a 30° lowering in the softening points of the polymers. Surprisingly, the *p-sec*-amylphenol polymer (polymer 24) which had the highest specific viscosity of all the isomeric amylphenol polymers had a softening point 60° lower than that of the *tert*-amylphenol polymer. From a consideration of molecular dimensions and bond angles, Megson (15) deduced that a Novolak resin must consist of highly kinked, asymmetrical molecules. He pointed out that a hardened resin has a sponge-like structure which can explain, partially, certain physical and chemical properties of the resin.

The infrared spectra of the *p*-alkylphenol–formaldehyde polymers are presented in Figs. 1 to 5. Compounds containing alkyl hydrocarbon groups usually exhibit absorption from 3130 to 2800 cm.$^{-1}$, which is the region attributed to the (C–H) stretching vibrations. Richards and Thompson (16) and Bender (2) have ascribed a weak absorption band at about 12.2 μ (820 cm.$^{-1}$) to 2,4-substitution of the phenolic ring. They suggest that a band at about 11.50 μ (870 cm.$^{-1}$) is characteristic of a 2,4,6-substituted phenol residue. On the basis of their work, one can conclude that most of the polymers studied having an alkyl side chain equal to or greater than four carbons had 2,4-substitution. All polymers which had a specific viscosity greater than 0.069 showed no band at 820 cm.$^{-1}$. It is interesting to note, however, that the *p*-cresol–formaldehyde polymer 1, which had a specific viscosity of 0.037, exhibited no band at 820 cm.$^{-1}$, whereas the *p*-isopropylphenol–formaldehyde polymer (No. 17), which had a specific viscosity of 0.069, absorbed in this region. This would indicate that one can not always correlate molecular size with 2,4-substitution, although it might be expected that polymers belonging to the series I which have the lowest molecular weight should have the highest concentration

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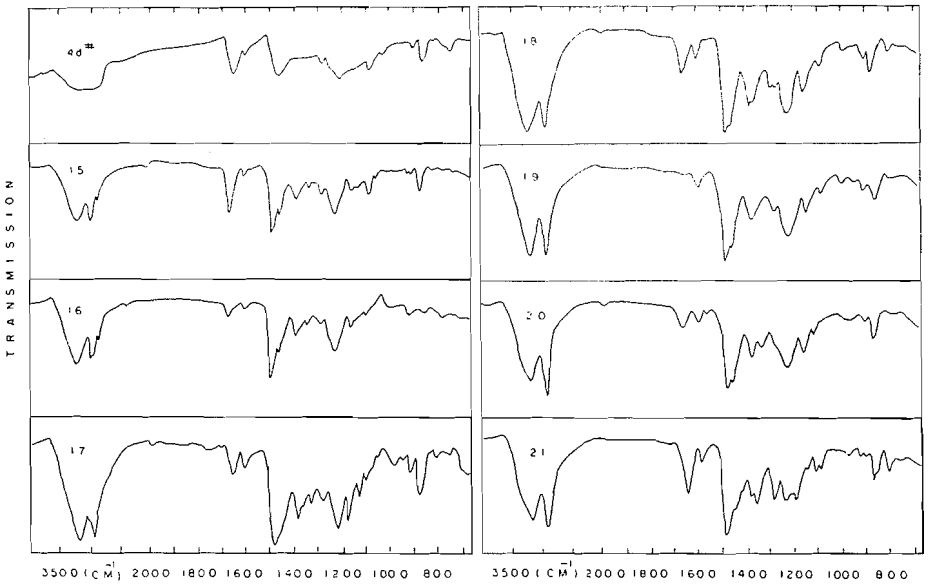

FIG. 2. Infrared spectra of *p*-alkylphenol–formaldehyde polymers:
4*d* *p*-Cresol–formaldehyde (insoluble fraction).
15 *p*-Ethylphenol–formaldehyde.
16 *p*-*n*-Propylphenol–formaldehyde.
17 *p*-Isopropylphenol–formaldehyde.

FIG. 3. Infrared spectra of *p*-alkylphenol–formaldehyde polymers:
18 *p*-*n*-Butylphenol–formaldehyde.
19 *p*-Isobutylphenol–formaldehyde.
20 *p*-*sec*-Butylphenol–formaldehyde.
21 *p*-*tert*-Butylphenol–formaldehyde.

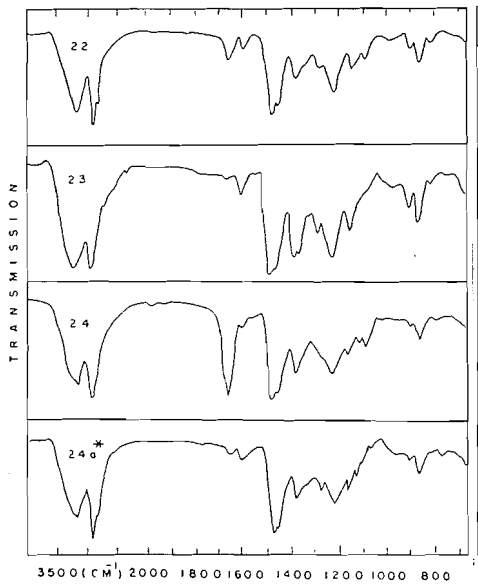

FIG. 4. Infrared spectra of *p*-alkylphenol–formaldehyde polymers:
22 *p*-*n*-Amylphenol–formaldehyde.
23 *p*-Isoamylphenol–formaldehyde.
24 *p*-*sec*-Amylphenol–formaldehyde.
24*a** *p*-*sec*-Amylphenol–formaldehyde (heat-treated).

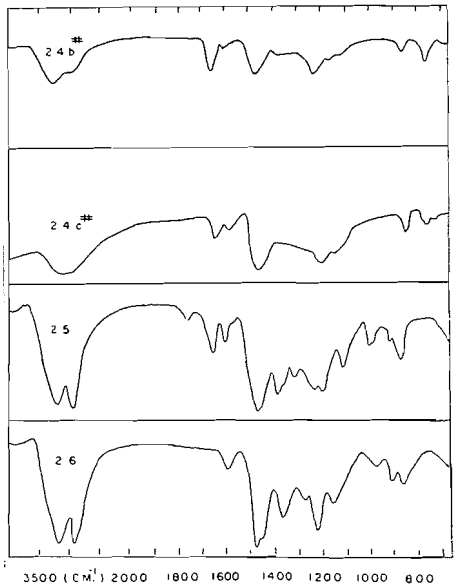

FIG. 5. Infrared spectra of *p*-alkylphenol–formaldehyde polymers:
24*b*** *p*-*sec*-Amylphenol–formaldehyde.
24*c*** *p*-*sec*-Amylphenol–formaldehyde (heat-treated).
25 *p*-*tert*-Amylphenol–formaldehyde.
26 *p*-*n*-Hexylphenol–formaldehyde.

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of 2,4-disubstituted end groups. It has been pointed out by Thompson and Torkington (19) that the characteristic frequencies shown by the substituted benzenes in the range of 715 to 880 cm.$^{-1}$ vary with the position of the substituents and are largely independent of their exact nature. The pronounced band at 860 to 875 cm.$^{-1}$ exhibited by all *p*-alkylphenol–formaldehyde polymers is attributed to 2,4,6-trisubstitution (16, 2). Absorption in the region of 3100 to 3300 cm.$^{-1}$ is characteristic of associated phenolic hydroxyl groups (16).

EXPERIMENTAL

1. Reagents

Bis-(2-ethoxyethyl) ether was purified and dried according to the procedure outlined in Vogel (21).

p-Cresol was distilled in vacuum and the middle fraction used.

p-Ethylphenol and *p*-*n*-propylphenol were prepared by the Martin modification (12, 21) of the Clemmensen reduction of purified *p*-hydroxyacetophenone and *p*-hydroxypropiophenone, respectively.

p-*n*-Butylphenol was prepared by sulphonating the pure hydrocarbon (21).

p-*n*-Hexylphenol was prepared according to the method of Sandulesco and Girard (17). The ester was first formed and then rearranged.

p-Isoamylphenol was prepared according to a modification of the procedure of Klages (11, 5).

The remaining chemicals used were obtained from Eastman Organic Chemicals, New York, and from Bios Laboratories, Inc., 17 West 60th Street, New York 23. They were checked for purity.

p-tert-Octylphenol was kindly donated by Rohm and Haas Company, Philadelphia 5, Pennsylvania, and was used without further purification.

2. Preparation of Polymers

Polymerizations of the p-alkylphenols and formaldehyde were carried out in pyrex combustion tubes having an inside diameter of 19 mm. The following procedure is representative of that used in all polymerizations.

To a mixture of purified *p*-cresol (10.813 gm., 0.100 mole) and *s*-trioxane (3.026 gm., 0.101 mole as formaldehyde) there was added a solution of 5 ml. of bis-(2-ethoxyethyl) ether containing 0.20 gm. of *p*-toluenesulphonic acid monohydrate. The reaction mixture (in the presence of nitrogen) contained in a sealed Carius tube was thoroughly mixed and heated in a Carius bomb furnace for 20 hr. at 130°.

After the *p*-alkylphenol–formaldehyde polymer was removed from the tube, it was air-dried and then finely pulverized. An amount of 4 gm. of the crude polymer (slightly colored) was added to 100 ml. of N,N-dimethylformamide and the mixture then heated at 80–90° for about 10 min. Undissolved polymer was removed by filtration with a coarse sintered glass funnel or filter paper. The clear filtrate was added dropwise with rapid stirring to 2 liters of water containing 5 ml. of concentrated hydrochloric acid (to cause settling of the polymer). The almost completely colorless polymer, removed by filtration, was then washed with water until free of chloride and dried at 60° under vacuum over phosphorus pentoxide.

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3. Viscosity Determinations of Polymers

All viscosities were carried out using a Fenske (A.S.T.M. No. 50) viscometer. The specific viscosity of 0.500 gm. of each dried polymer in 100 ml. of N,N-dimethylformamide at 25° (±0.05°) was taken.

4. Softening Points of Polymers

The softening points of the polymers were taken in capillary tubes which were heated in a copper melting point block fitted with a light and lens for illumination and observation (7). The approximate softening point of each polymer was determined by raising the temperature of the melting point block by 5° intervals and noting the temperature interval in which a new sample softened in one minute. The softening points recorded are those at which all of each polymer fully underwent a change in physical state. Part of the polymer usually softened at a temperature considerably lower than that reported. When the polymers were heated gradually, no softening points could be obtained. No claim to quantitative accuracy of the softening points of the polymers is made.

5. Infrared Spectrophotometric Analyses

A Perkin-Elmer Model 21 double-beam recording spectrophotometer with a sodium chloride prism was used to obtain the spectra presented in Figs. 1 to 5. Most of the samples were run as 5% solutions in chloroform. Any polymer samples which were partially soluble in chloroform were also run as Nujol mulls and are so noted on the spectra concerned.

The authors are indebted to the British Columbia Research Council for the infrared analyses.

SUMMARY

Polymerization of *p*-cresol with formaldehyde in sealed tubes resulted in polymers having almost double the molecular weight of those obtained in open systems. In closed systems higher molecular weight polymers were obtained from *p-sec*-butylphenol and *p-sec*-amyphenol than from *p*-cresol. A polymer obtained from *p-sec*-amyphenol and formaldehyde (η_{sp} 0.112) was found to be much more stable to heat than one from *p*-cresol–formaldehyde (η_{sp} 0.091). Infrared studies of the polymers showed that two of the absorption bands present in the original *p*-cresol–formaldehyde polymer (at 1095 and 1670 $cm.^{-1}$) were not present in the spectrum of the same polymer subsequently heated at 182° for three hours. The spectra of the original and heat-treated *p-sec*-amylphenol–formaldehyde polymers were essentially the same.

ACKNOWLEDGMENT

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NOTE

SUR LE SPECTRE ULTRAVIOLET DE L'ACIDE PERACÉTIQUE ET L'HYDROLYSE DES PERACÉTATES

PAR PAUL A. GIGUÈRE ET A. W. OLMOS[1]

Il ne semble pas exister dans la littérature de données précises sur l'absorption ultraviolette de l'acide peracétique. Egerton et ses collaborateurs (2) rapportent avoir mesuré l'absorption d'une solution à 75% et l'avoir trouvée à peu près égale à celle de l'acide acétique, ce qui paraît surprenant a priori étant donné la grande opacité du groupement peroxydique dans l'ultraviolet. Comme nous avions déjà préparé ce composé à un assez haut degré de pureté afin d'étudier sa structure moléculaire au moyen de l'infrarouge (4) nous avons jugé bon de mesurer en même temps son spectre ultraviolet.

La préparation de l'acide peracétique à 97% a déjà été décrite en détail. La soude qui servit à neutraliser les solutions fut préparée à partir de sodium métallique et d'alcool éthylique absolu; le produit de l'hydrolyse était ensuite dosé par l'acide phtalique solide. En général les solutions semblaient parfaitement stables, même sous l'action de l'ultraviolet dans le spectrophotomètre (Modèle DU de Beckman). L'apparition occasionnelle de bulles d'oxygène sur les parois de la cuvette d'absorption entrainait inévitablement le rejet de l'échantillon. Toutes les mesures furent faites avec des solutions fraîchement préparées et chaque spectre fut enregistré deux fois afin de s'assurer qu'il ne se produisait aucune décomposition appréciable.

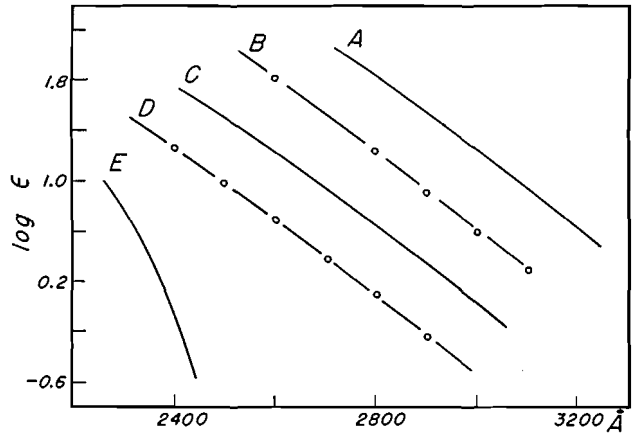

FIG. 1. Absorption ultraviolette de solutions d'acide peracétique et de peracétates. A. Ion perhydroxyle. B. Ion peracétate. C. Peroxyde d'hydrogène. D. Acide peracétique. E. Acide acétique.

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Les courbes de la figure 1 donnent les coefficients d'extinction d'après la loi de Beer, $\log I/I_0 = -\epsilon\, c\, d$, où les concentrations, c, sont en moles par litre et l'épaisseur de l'échantillon, d, est en cm. Comme pour le peroxyde d'hydrogène, dont le spectre bien connu (6) est reproduit ici pour fin de comparaison, l'absorption ultraviolette de l'acide peracétique ne présente qu'un seuil continu sans aucune indication de maximum. Il en est de même des ions correspondants, O_2H^- et CH_3COOO^-, dont l'absorption est toutefois beaucoup plus forte que celle des molécules non dissociées. On sait par ailleurs que les solutions de soude sont transparentes jusqu'à 2300 Å environ.

L'acide peracétique dissous dans un solvant indifférent (iso-octane) absorbe presque de la même façon qu'en solution aqueuse, ce qui confirme bien que les peracides sont des acides assez faibles. En effet, Everett et Minkoff (3) ont trouvé récemment par titration potentiométrique une valeur de 8.2 pour le pK de l'acide peracétique. Ce résultat est en tout point conforme aux nôtres, comme le montrent les données du tableau I, où les pH de solutions partiellement neutralisées ont été calculés à partir de l'équation de Henderson, d'abord d'après la composition,

TABLEAU I

pH DES SOLUTIONS DE PERACÉTATES ALCALINS

Base / Acide	pH, d'après la composition	ϵ	pH, d'après l'absorption
0	4.7	2.58	—
0.05	6.9	3.75	6.9
0.1	7.2	4.97	7.1_5
0.2	7.6	6.97	7.4
0.3	7.8	10.8	7.7_5
0.5	8.2	17.0	8.2_5
0.7	8.5_5	23.1	8.5
1.0	10.4	33.6	—

$$\mathrm{pH} = \mathrm{p}K + \log([\mathrm{sel}]/[\mathrm{acide}]) \qquad [1]$$

puis d'après les coefficients d'extinction ϵ à 2700 Å,

$$\mathrm{pH} = \mathrm{p}K + \log[(\epsilon - \epsilon_{HA})/(\epsilon_{A^-} - \epsilon)], \qquad [2]$$

ϵ_{HA} étant le coefficient correspondant de l'acide pur (en solution environ 0.08 molale) et ϵ_{A^-}, celui du mélange équimoléculaire soude-acide.

A la suite de leurs travaux sur la vitesse d'oxydation de l'acide *O*-iodobenzoique par l'acide peracétique Boëseken et Wicherlink (1) ont conclu que la décomposition de ce dernier par un excès de base caustique procède en deux étapes:

$$CH_3COOOH + NaOH \rightarrow CH_3COONa + H_2O_2 \qquad [3]$$

et

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2}O_2. \qquad [4]$$

Dans les conditions de leurs expériences, soit par addition de 5 à 10 cc. de soude (variant de 20 à 50%) à 1 cc. d'acide peracétique à 10%, l'hydrolyse

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[3] semblait complète en quelques minutes tandis que la décomposition du peroxyde d'hydrogène était alléatoire. Leur conclusion était basée sur le fait que ces solutions ne libéraient pas d'iode lors de l'addition d'une solution acide de KI, réaction connue sous le nom de Riesenfeld-Liebhafsky (6). Il est maintenant évident qu'une telle conclusion est erronée. En effet, si l'hydrolyse était aussi rapide que prétendu, les courbes d'absorption de solutions de peracide partiellement neutralisées ne devraient pas dépasser celles du peroxyde d'hydrogène (courbe C, Fig. 1). Bien plus, nous avons trouvé que l'addition d'un grand excès de soude (6:1) à l'acide peracétique n'augmente pas le coefficient d'absorption au delà de la courbe C alors que dans l'hypothèse de l'hydrolyse [3] l'absorption devrait tendre vers celle de l'ion O_2H^- (courbe A). Récemment, Partington et Fathallah (5) ont prouvé qu'un test de Riesenfeld-Liebhafsky *négatif* n'est pas valide dans le cas des perborates et des percarbonates; nos résultats confirment bien qu'il en est de même pour les peracétates.

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THE PREPARATION OF D-*ARABO*PENTURONIC ACID AND D-*THREO*- AND D-*ERYTHRO*-TETRURONIC ACIDS[1]

BY P. A. J. GORIN[2] AND A. S. PERLIN

ABSTRACT

D-Glucurono-γ-lactone, D-galacturonic acid, and potassium D-glucuronate have been degraded in good yield to D-*arabo*penturonic, D-*threo*tetruronic, and D-*erythro*tetruronic acids, respectively, using lead tetraacetate in acetic acid solvent as the reagent.

INTRODUCTION

Earlier papers (11, 12) have described lead tetraacetate as a reagent useful for the stepwise degradation of sugars. It has been shown, for example, that D-glucose and L-sorbose may be degraded respectively to D-erythrose and L-glyceraldehyde in excellent yield. In the present paper it is shown that a similar reaction can be utilized as a convenient method for preparing D-*arabo*-penturonic acid and D-*erythro*- and D-*threo*-tetruronic acids from the related higher-order member of the series. D-*Arabo*penturonic acid and its barium salt have been prepared by Machida (8) from 2,3-*O*-isopropylidene-D-mannono-γ-lactone by lead tetraacetate oxidation followed by acid hydrolysis. D-*Erythro*-tetruronic acid (3) and L-*threo*tetruronic acid (4) have been shown to be present in the ozonolysis products of the enol of 5-keto-4-deoxy-D-mannosaccharo-3,6-γ-lactone and the corresponding D-gluco-derivative, respectively. The 2,3-di-*O*-acetyl methyl ester of the latter uronic acid has also been reported (7).

Trial experiments showed that D-glucurone in acetic acid containing a little water (1) rapidly consumed one mole of lead tetraacetate oxidant. Under similar conditions D-galacturonic acid took up 2.2 moles and potassium D-glucuronate 1.9 moles of oxidant; thereafter the uptakes of the oxidizing agent were relatively slow. These amounts of lead tetraacetate consumed during the initial rapid stage of the reaction were consistent with virtually stoichiometric conversion of the compounds to penturonic and tetruronic acids. Accordingly, the oxidations were repeated on a preparative scale.

The product from D-glucurone (I), after oxidation with one mole of lead tetraacetate followed by hydrolysis of the formate ester group, was shown

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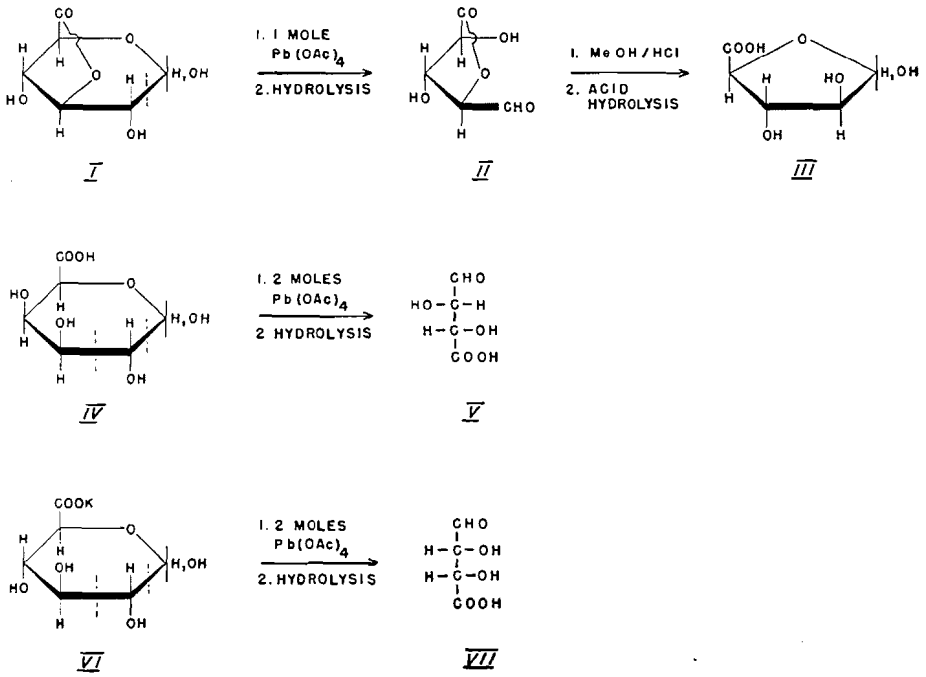
[2]*National Research Council of Canada Postdoctorate Fellow, 1955–56.*

to contain both D-*arabo*penturono-lactone (II) and D-*arabo*penturonic acid (III). This mixture was characterized as follows: reaction of the mixture with diazomethane in ethereal methanol gave a sirupy mixture of methoxyl content 6.9%, corresponding to 0.35 equivalents of free acid and 0.65 equivalents of lactone in the original oxidation product. Also, reduction of the lactone–acid mixture gave mainly crystalline D-arabitol (13) and a trace of D-lyxono-γ-lactone (detected on a paper chromatogram). Treatment of the oxidation product with acetone containing a little sulphuric acid followed by methylation with diazomethane in methanol–ether gave, in small yield, a crystalline material which was identified as 1,2-*O*-isopropylidene-D-*arabo*-penturonic acid methyl ester. The above mixture with hot methanolic hydrogen chloride gave methyl-D-*arabo*pentofururonoside methyl ester which was purified by distillation. Sirupy D-*arabo*penturonic acid could be obtained from this substance by hydrolysis with hot aqueous formic acid and was characterized by conversion with aqueous sodium borohydride to crystalline D-lyxono-γ-lactone (2). The structure of the methyl ester fururonoside was confirmed by reduction with aqueous sodium borohydride to methyl-αβ-D-arabofuranoside which was hydrolyzed in hot aqueous formic acid to D-arabinose, characterized as its crystalline toluene-*p*-sulphonylhydrazone (6).

D-Galacturonic acid (IV) was oxidized with two moles of lead tetraacetate. The product appeared to be a monoformate ester from its characteristic infrared spectrum, with strong peaks at 1725^{-1} and 1170^{-1} cm. (15), and from alkaline saponification data. Since hydrolysis of the formate ester derivative occurred on standing, it is possible that the oxidation product originally



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contained more than one formate group and partly hydrolyzed before the reaction mixture could be worked up. A separate oxidation under similar conditions, followed by hydrolysis of the formate esters, furnished in very good yield D-*threo*tetruronic acid (V) which gave a single spot on a paper chromatogram with the *p*-anisidine hydrochloride spray (5). Its R_F value was less than D-*arabo*penturonic acid, thus suggesting that the tetruronic acid exists in solution as the dimer. The uronic acid was characterized as its crystalline 2,4-dinitrophenylhydrazone and by conversion on sodium borohydride reduction to D-threonolactone which gave crystalline D-threonic acid phenylhydrazide after treatment with ethanolic phenylhydrazine (9). Methanolic hydrogen chloride reacted with D-*threo*tetruronic acid to give the methyl ester dimethyl acetal, which was purified by distillation.

Oxidation of potassium D-glucuronate (VI) in acetic acid with two moles of lead tetraacetate afforded, in about 50% yield, a product which contained mainly D-*erythro*tetruronic acid (VII). On a paper chromatogram the tetruronic acid moved at practically the same speed as D-*threo*tetruronic acid and thus also appears to be dimeric in solution. A small proportion of a faster moving compound, probably due to overoxidation, was shown to be present. The uronic acid was characterized by reduction with aqueous sodium borohydride, to give crystalline L-erythrono-γ-lactone (14). Also, cold methanolic hydrogen chloride converted the tetruronic acid to the methyl ester dimethyl acetal which could be purified by distillation.

EXPERIMENTAL

Paper chromatography was carried out on Whatman No. 1 filter paper using *n*-butanol–ethanol–water (40:11:19 v/v) and ethyl acetate – acetic acid – formic acid – water (18:3:1:4 v/v) as solvents. The terms R_{gal}, R_{rh} are used to denote distances travelled on the paper chromatogram by a compound relative to galactose and rhamnose, respectively. Evaporations were carried out under reduced pressure at 40°C. Optical rotations were measured at 27°C.

Oxidation of D-*Glucurono-γ-lactone with Lead Tetraacetate*

D-Glucurone (25 mgm.) was dissolved in water (0.2 cc.) and added to acetic acid (25 cc.). The solution was treated with a 1% solution of lead tetraacetate in acetic acid (25 cc.). At intervals aliquots (3 cc.) of the mixture were removed and added to an aqueous solution (10 cc.) containing potassium iodide (0.7 gm.) and sodium acetate (4 gm.). The iodine liberated was titrated with 0.1 *N* sodium thiosulphate. A blank determination was also carried out. The following results were obtained:

Oxidation time (min.)	2	5	10	30	60	131
Molar uptake of lead tetraacetate	0.99	1.01	1.04	1.08	1.18	1.40

On a preparative scale finely powdered D-glucurone (3.56 gm.) was stirred vigorously in a solution of lead tetraacetate (12.6 gm.; 1.4 equivalents) in acetic acid (350 cc.). After six minutes the suspension had dissolved and 10%

oxalic acid in acetic acid (30 cc.) was added to decompose excess oxidant. After it was stirred for 30 min. the solution was filtered and the filtrate evaporated to a sirup which was dissolved in water (50 cc.). After 18 hr. the solution was treated with Amberlite IR-120 and evaporated to a sirup (3.23 gm.). The product, detected by the *p*-anisidine hydrochloride spray (5) after running on a paper chromatogram in the acidic solvent, gave much streaking, perhaps because of the ready conversion of the lactonic material to the free D-*arabo*-penturonic acid. The sirup had, on successive days, $[\alpha]_D$ +57°, +55°, +52°, +51°, and +49° (*c*, 3.43, water).

To determine the proportion of lactone to free acid in the mixture the sirup (293 mgm.) was dissolved in methanol (30 cc.) and ethereal diazomethane added until the yellow color persisted. The solution was evaporated to a sirup which was dissolved in acetone. A little insoluble material was filtered off and the filtrate was evaporated to a sirup (282 mgm.) which had –OMe 6.9%. This value corresponds to 0.35 equivalents of free acid and 0.65 equivalents of lactone in the starting material. When the sirup was run on a paper chromatogram using the neutral solvent two spots with R_{rh} 1.26 and R_{rh} 1.48 of roughly equal intensity were detected by spraying with ammoniacal silver nitrate (10).

D-*Arabitol*

The lead tetraacetate oxidation product from D-glucurone (264 mgm.) in water (10 cc.) was treated dropwise with a solution of sodium borohydride (150 mgm.) in water (10 cc.). After 18 hr. excess reductant was destroyed with acetic acid, the solution was passed through a column of Amberlite IR-120 and evaporated to dryness. The residue was dissolved in methanol and the solution evaporated to a sirup, the process being repeated six times in order to remove boric acid as volatile methyl borate. The product (245 mgm.) gave, on a paper chromatogram run with the ethyl acetate – acetic acid – water (9:2:2 v/v) solvent, a strong spot (R_{gal} 1.4) corresponding to arabitol and a small one (R_{gal} 2.0) corresponding to lyxono-γ-lactone (ammoniacal silver nitrate spray). It crystallized and was recrystallized twice from ethyl acetate – methanol and then from ethanol. The crystals (72 mgm.), m.p. 99–101°C., $[\alpha]_D$ +7° (*c*, 11.0, saturated aqueous borax), undepressed on admixture with authentic D-arabitol, gave the same X-ray powder diagram as D-arabitol. Calculated for $C_5H_{12}O_5$: C, 39.47%, H, 7.95%; found: C, 39.43%, H, 7.99%.

*1,2-O-Isopropylidene-*D*-arabopenturonic Acid Methyl Ester*

The *arabo*penturonic acid – lactone mixture (145 mgm.) was shaken for 18 hr. in acetone (20 cc.) containing sulphuric acid (0.1 cc.). The solution was neutralized with barium carbonate, filtered, and evaporated to a white solid. The residue was dissolved in water, treated with Amberlite IR-120, and the solution evaporated to a sirup (178 mgm.). The product was dissolved in methanol and treated with ethereal diazomethane until the yellow color persisted. The solvents were evaporated off and the resulting sirup (192 mgm.) partly crystallized. The crystals were isolated and recrystallized from ether–pentane to give long colorless prisms (26 mgm.), m.p. 133–134°C., $[\alpha]_D$ +67°

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(*c*, 1.0, ethanol); non-reducing to Fehling's solution. Calculated for $C_9H_{14}O_6$: C, 49.54%, H, 6.47%; found: C, 49.62%, H, 6.36%. The poor yield is probably accounted for by the small proportion of free D-*arabo*penturonic acid present in the starting material.

Methyl D-*Arabopentofururonoside Methyl Ester*

The sirup containing D-*arabo*penturonic acid and its lactone (291 mgm.) was dissolved in 0.5% methanolic hydrogen chloride (5 cc.) and refluxed for five minutes. The solution was neutralized (Ag_2CO_3) and evaporated to a sirup (339 mgm.), which did not reduce Fehling's solution. Distillation (bath temperature 140°C. at 1 mm.) gave the methyl ester glycoside as a sirup (83% of sirup distilled), n_D^{21} 1.4723, $[\alpha]_D$ +19° (*c*, 2.9, ethanol). Calculated for $C_7H_{12}O_6$: C, 43.75%, H, 6.29%, –OMe, 32.3%; found: C, 44.10%, H, 6.23%, –OMe, 33.3%.

D-*Arabopenturonic Acid*

The methyl ester methyl fururonoside (127 mgm.) was converted to D-*arabo*penturonic acid by heating at 100°C. for 10 hr. in water (2 cc.) containing formic acid (0.2 cc.). The solution was evaporated to a sirup (105 mgm.), $[\alpha]_D$ +22° (*c*, 2.6, water), which gave on a paper chromatogram (acid solvent) a gray-brown spot with R_{rh} 0.42 using the *p*-anisidine hydrochloride spray.

D-*Lyxono-γ-lactone*

D-*Arabo*penturonic acid obtained by acid hydrolysis of its methyl ester methyl fururonoside (134 mgm.) was dissolved in water (10 cc.) and added to an aqueous solution (10 cc.) of sodium borohydride (250 mgm.). After 18 hr. the reaction mixture was worked up as in the preparation of arabitol (above) and the final sirup was heated at 100°C. for six hours to promote lactonization. On a paper chromatogram (neutral solvent; ammoniacal silver nitrate spray) the product showed mainly lyxono-γ-lactone and a trace of material corresponding to arabitol. The sirup crystallized and it was recrystallized thrice from ethyl acetate. Yield 23 mgm., m.p. and mixed m.p. 108–110°C., and $[\alpha]_D$ +70° (*c*, 4.0, water). The product gave an X-ray diffraction pattern similar to that of D-lyxono-γ-lactone. Calculated for $C_5H_8O_5$: C, 40.54%, H, 5.44%; found: C, 40.67%, H, 5.49%.

D-*Arabinose*

The distilled methyl ester of methyl-D-*arabo*pentofururonic acid (158 mgm.) in ice cold water (10 cc.) was added during 10 min. to ice cold aqueous sodium borohydride (200 mgm. in 10 cc.). After 18 hr. at 0°C. and 10 hr. at 27°C. the reduction product was isolated as in the preparation of arabitol and the free carboxyl groups were esterified with ethereal diazomethane. A second treatment of the methyl ester with sodium borohydride was then carried out. The final product was dissolved in water, passed through IR4B to remove the unchanged acid, and evaporated to a sirup (116 mgm.). On a paper chromatogram (neutral solvent) it moved with R_{rh} 1.2 (spray: ammoniacal silver nitrate). On detection with the *p*-anisidine hydrochloride spray a pink spot of similar speed was observed. It corresponded to methyl-αβ-arabofuranoside.

The methyl-$\alpha\beta$-D-arabofuranoside (116 mgm.) was hydrolyzed in water (4 cc.) containing formic acid (1 cc.) at 100°C. for two hours. The solution was evaporated to a sirup which was dissolved in water and kept at 100°C. for two hours to hydrolyze formate esters. On evaporation the sirup obtained (105 mgm.) was found by paper chromatography to contain only arabinose (neutral solvent; sprays: *p*-anisidine hydrochloride and ammoniacal silver nitrate). The sirup crystallized and the material was twice recrystallized from ethanol. Yield 30 mgm., m.p. *ca.* 147°C.

Since the melting point of the D-arabinose was low, it (16 mgm.) was refluxed for 30 min. in methanol (10 cc.) containing toluene-*p*-sulphonylhydrazine (1.2 equivalents; 24 mgm.). The product was recrystallized from methanol. Yield 10 mgm., m.p. and mixed m.p. 150–152°C. Calculated for $C_{12}H_{18}O_6N_2S$: C, 45.28%, H, 5.70%; found: C, 45.27%, H, 5.705%. The crystals gave an X-ray powder diagram which was identical with that of authentic D-arabinose toluene-*p*-sulphonylhydrazone.

D-Threotetruronic Acid

The rate of reaction of lead tetraacetate with D-galacturonic acid in acetic acid was followed in the manner described for the oxidation of D-glucurone. The following results were obtained:

Oxidation time (min.)	2	5	10	30	60	131
Molar uptake of lead tetraacetate	2.22	2.26	2.33	2.49	2.88	3.53

On a larger scale, D-galacturonic acid monohydrate (860 mgm.) in water (2 cc.) and acetic acid (100 cc.) was stirred vigorously with lead tetraacetate (3.6 gm.; 2 equivalents). After two minutes the solution had cleared and no oxidant remained. Water (100 cc.) was added followed by 10% oxalic acid in acetic acid (8.2 cc.). The precipitate which formed was filtered off with the aid of Celite and the filtrate was evaporated to a sirup which was dissolved in water (25 cc.). After 18 hr. the solution was passed through Amberlite IR-120 and the eluate evaporated to a friable light yellow solid (530 mgm.) with $[\alpha]_D$ $-11° \rightarrow +3°$ (18 hr.; constant value; *c*, 2.3, water). On a paper chromatogram (acidic solvent; spray: *p*-anisidine hydrochloride) a yellow-brown spot of R_{gal} 1.3 was obtained.

Formate Ester of D-Threotetruronic Acid

D-Galacturonic acid was oxidized with lead tetraacetate using the same amounts and conditions as above. Remaining excess lead was removed from the acetic acid solution by stirring with Amberlite IR-120 until no precipitate was produced on addition of oxalic acid in acetic acid. The mixture was evaporated to a sirup which was dissolved in ethyl acetate. A little insoluble material was separated by filtration and the filtrate was evaporated to a sirup which was kept overnight at 1 mm. pressure over potassium hydroxide. The product (497 mgm.) absorbed strongly in the infrared region at 1725 cm.$^{-1}$ and 1170 cm.$^{-1}$, characteristic of formate esters (1723 cm.$^{-1}$ and 1170–1200 cm.$^{-1}$) and was shown by saponification with alkali to contain 1.0 formate ester group, assuming a molecular weight of 162.

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D-*Threotetruronic Acid 2,4-Dinitrophenylhydrazone*

The tetruronic acid (138 mgm.) was refluxed for 18 hr. in ethanol (40 cc.) containing 2,4-dinitrophenylhydrazine (204 mgm.; 1 equivalent) and acetic acid (1 cc.) and the solution was then evaporated to dryness. The residue was dissolved in warm aqueous ethanol from which crystals separated on cooling. Recrystallization from the same solvent gave ochre crystals (116 mgm.), m.p. 111–113°C. Calculated for $C_{10}H_{10}O_8N_4$: C, 38.22%, H, 3.21%; found: C, 37.99%, H, 3.165%.

D-*Threonic Acid Phenylhydrazide*

The tetruronic acid (140 mgm.) in water (10 cc.) was added to a solution of sodium borohydride (250 mgm.) in water (10 cc.). After 18 hr. reaction time the sirupy product (117 mgm.), isolated by the procedure described in the preparation of arabitol, was heated at 100°C. for eight hours in order to promote lactonization; it did not crystallize. On a paper chromatogram (neutral solvent; ammoniacal silver nitrate spray) the major spot had R_{rh} 1.3, and a fainter spot with R_{gal} <1, corresponding to unchanged acid, was also present. A portion of the sirup (58 mgm.) was refluxed for two minutes in ethanol (0.2 cc.) containing phenylhydrazine (36 mgm.) and then kept for 24 hr. at room temperature. The solution deposited crystals which were recrystallized from ethanol. Yield 15 mgm., m.p. 156–157.5°C. (D-erythronic acid phenylhydrazide (14) has m.p. 128°C.), and $[\alpha]_D$ −35° (*c*, 4.2, ethanol). Calculated for $C_{10}H_{14}O_4N_2$: C, 52.93%, H, 6.21%; found: C, 53.09%, H, 6.24%.

D-*Threotetruronic Acid Methyl Ester Dimethyl Acetal*

The tetruronic acid (201 mgm.) was refluxed for two minutes in 1% methanolic hydrogen chloride (10 cc.) and allowed to stand at room temperature for 18 hr. The solution was neutralized (Ag_2CO_3), filtered, and evaporated to a sirup which was distilled (bath temperature 120°C. at 1 mm.). The resulting sirup (177 mgm.) had $[\alpha]_D$ −27° (*c*, 2.3, ethanol) and n_D^{21} 1.4501. Calculated for $C_7H_{14}O_6$: C, 43.29%, H, 7.27%, $-OCH_3$, 46.9%; found: C, 43.42%, H, 7.25%, $-OCH_3$, 46.2%.

D-*Erythrotetruronic Acid*

The rate of oxidation of potassium D-glucuronate with $Pb(OAc)_4$ in acetic acid was followed using the method described for the oxidation of D-glucurone. The following results were obtained:

Oxidation time (min.)	2	4	7	15	22
Molar uptake of lead tetraacetate	1.92	2.16	2.37	2.53	2.62

Potassium D-glucuronate (1.76 gm.) in water (2 cc.) was mixed with acetic acid (200 cc.), and lead tetraacetate (7.4 gm.; 2.2 equivalents) added with vigorous stirring. When the lead tetraacetate had dissolved, water (200 cc.) was added followed by 10% oxalic acid in acetic acid (17.6 cc.). The precipitate was filtered off, and the filtrate evaporated to a sirup which was dissolved in water (25 cc.). After 18 hr. the solution was passed through Amberlite IR-120 and the eluate evaporated to a sirup (516 mgm.), $[\alpha]_D$ +16° → +18° (18 hr.;

constant value; *c*, 2.32, water). On a paper chromatogram (acidic solvent; *p*-anisidine hydrochloride spray) the main spot was yellow-brown, with R_{gal} 1.4 and also there was a reddish brown spot of R_{rh} 1.3.

D-*Erythrono-γ-lactone*

The tetruronic acid (106 mgm.) was reduced with aqueous sodium borohydride as described for the preparation of D-threonolactone from D-*threo*-tetruronic acid. The sirupy product (93 mgm.) crystallized after distillation (1 mm. pressure). The distillate, on a paper chromatogram (neutral solvent; ammoniacal silver nitrate spray), gave a single spot corresponding to erythrono-γ-lactone. The crystals were separated by tiling and were recrystallized twice from benzene–ethanol. Yield 7 mgm., m.p. 99–102°C., $[\alpha]_D$ +73° (*c*, 1.3, water). Calculated for $C_4H_6O_4$: C, 40.68%, H, 5.12%; found: C, 40.73%, H, 5.19%. The X-ray diffraction pattern of the product was identical with that of D-erythrono-γ-lactone.

D-*Erythrotetruronic Acid Methyl Ester Dimethyl Acetal*

The sirupy tetruronic acid (230 mgm.) was dissolved in 1% methanolic hydrogen chloride (5 cc.) which was then refluxed for a few seconds and left at 27°C. for 24 hr. The solution was neutralized (Ag_2CO_3), filtered, and evaporated to a sirup which was distilled at 1 mm. pressure (bath temperature 120°C.) to give a sirup (175 mgm.), n_D^{21} 1.4557 and $[\alpha]_D$ +40° (*c*, 2.7, ethanol). Calculated for $C_7H_{14}O_6$: C, 43.29%, H, 7.27%, $-OCH_3$, 46.9%; found: C, 43.27%, H, 7.23%, $-OCH_3$, 46.9%.

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FREE RADICALS BY MASS SPECTROMETRY

XI. THE MERCURY PHOTOSENSITIZED DECOMPOSITION OF C_2–C_4 OLEFINS[1]

By F. P. Lossing, D. G. H. Marsden,[2] and J. B. Farmer[2]

ABSTRACT

The mercury photosensitized (Hg^3P_1) decomposition of olefins has been examined using a reactor coupled directly to a mass spectrometer. The primary split of ethylene has been shown to be predominantly molecular, and that of propylene mainly into an allyl radical and a hydrogen atom. With 1-butene the split is predominantly at a C–C bond giving allyl and methyl radicals, although a rupture of a C–H bond occurs as well. With 2-butene and isobutene a C–H bond is broken. It is concluded that the allyl and methallyl radicals produced have large cross sections for reaction with excited mercury atoms.

INTRODUCTION

The use of mass spectrometers to detect free radicals in reacting systems has been described by a number of authors and has been reviewed in some detail in two recent publications (24, 26). The radicals have been produced by various means: pyrolysis in furnaces and on hot filaments, by reactions of hydrogen atoms, and in combustion flames. Although some 25 free radicals have been detected in pyrolytic reactions, the temperatures used in the production of the radicals are usually so high that only radicals with considerable thermal stability can be studied. In addition, the reactions of such radicals that are stable enough to be investigated are those corresponding to much higher temperatures than are customary in kinetic studies. It would be a great advantage if a means of producing radicals at lower temperatures could be employed.

NH_2 radicals and CN radicals have been detected in a continuously irradiated flow system by photographing the absorption spectrum (23). The absorption coefficients of most organic compounds are so small, however, that at low pressures very little energy is absorbed by a reactant which is flowing rapidly through an illuminated zone of reasonable proportions. The use of external reflectors to increase the path length is of little advantage at these pressures since the wall of the reaction vessel absorbs much more radiation than the reactant.

This difficulty could be overcome in part by taking advantage of the large absorption coefficient of mercury vapor for radiation of 2537 Å, as has been done in studies of photosensitized reactions. Preliminary work (8) has shown that mercury photosensitization permits the absorption of sufficient quanta to dissociate acetone in a fast flow system. At a partial pressure of a few microns in a stream of helium at 8 mm., acetone was dissociated to the extent of 50–80% in 0.002 sec. The detection of CH_3CO radicals as well as CH_3 radicals showed that relatively unstable radicals could be produced in appreciable amounts.

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In the present work an attempt has been made to use this technique to determine the primary products of dissociation of C_2–C_4 olefins upon collision with $Hg(^3P_1)$ atoms. The reaction conditions are much different from those ordinarily used in photosensitized studies, the partial pressure of reactant being only a few microns and the partial pressure of mercury much higher. The incident flux is greater than is customary. A large excess of helium is present. These factors make conditions more favorable for determining the primary step, but the subsequent reaction products may be quite different from those found at higher pressures and lower intensities.

Previous work on the photosensitized decomposition of olefins has been reviewed in detail (17, 26) and only a brief summary will be given here.

For ethylene a molecular split has been suggested (28) and a mechanism involving an excited ethylene molecule has been proposed (18):

$$C_2H_4 + Hg(^3P_1) \rightarrow C_2H_4^* + Hg(^1S_0) \quad [1]$$

$$C_2H_4^* \rightarrow C_2H_2 + H_2 \quad [2]$$

$$C_2H_4^* + C_2H_4 \rightarrow 2C_2H_4. \quad [3]$$

An alternative primary split is one leading to a vinyl radical and H atom (16):

$$C_2H_4 + Hg(^3P_1) \rightarrow C_2H_3 + H + Hg(^1S_0). \quad [4]$$

Evidence for the occurrence of reaction [4] has been found at 300°C. (19) but at lower temperatures the evidence supports the split by reactions [1] and [2]. The predominance of reactions [1] and [2] over reaction [4] has been recently demonstrated quite convincingly using mixtures of C_2H_4 and C_2D_4 (2, 4). There is evidence that the detailed reaction is more complex than written above (5, 2, 3).

The mercury photosensitized decomposition of propylene appears to proceed by the following mechanism (10):

$$C_3H_6 + Hg(^3P_1) \rightarrow C_3H_6^* + Hg(^1S_0) \quad [5]$$

$$C_3H_6^* \rightarrow C_3H_5 + H \quad [6]$$

$$C_3H_6^* + C_3H_6 \rightarrow 2C_3H_6. \quad [7]$$

The absence of an initial pressure rise led these authors to the conclusion that reaction [6] predominated over the analogue of reaction [2], presumably as a result of the weaker C–H bond in propylene. Although the quenching cross-section for propylene is slightly larger than for ethylene (6) the quantum yield is only about one-half that of ethylene (26).

The mercury photosensitized decompositions of the butenes have not been studied in as much detail. The main products of the reaction of 1-butene were 2-butene and a liquid polymer (12). At low pressures other products were found and the following mechanism was proposed:

$$1\text{-}C_4H_8 + Hg(^3P_1) \rightarrow 1\text{-}C_4H_8^* + Hg(^1S_0) \quad [8]$$

$$1\text{-}C_4H_8^* \rightarrow C_4H_7 + H \quad [9]$$

$$1\text{-}C_4H_8^* + 1\text{-}C_4H_8 \rightarrow 2\text{-}C_4H_8 + 1\text{-}C_4H_8. \quad [10]$$

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The reaction of $Hg(^3P_1)$ atoms with 2-butene was found to be similar except that no isomerization to 1-C_4H_8 occurred (12). In the mercury photosensitized reaction of isobutene, a complex mixture of products was found (11, 1) and the following mechanism was suggested:

$$\text{iso-}C_4H_8 + Hg(^3P_1) \rightarrow \text{iso-}C_4H_8^* + Hg(^1S_0) \quad [11]$$

$$\text{iso-}C_4H_8^* \rightarrow \text{products} \quad [12]$$

$$\text{iso-}C_4H_8^* + \text{iso-}C_4H_8 \rightarrow 2\ \text{iso-}C_4H_8. \quad [13]$$

The nature of the products of reaction [12] could not be determined. A liquid polymer was found and was attributed to the following reaction:

$$\text{iso-}C_4H_8^* + \text{iso-}C_4H_8 \rightarrow C_8H_{16}. \quad [14]$$

EXPERIMENTAL

The Reactor

A diagram of the reaction system used is given in Fig. 1. It consisted of a mercury saturator, a reaction zone, and a low pressure mercury lamp. The

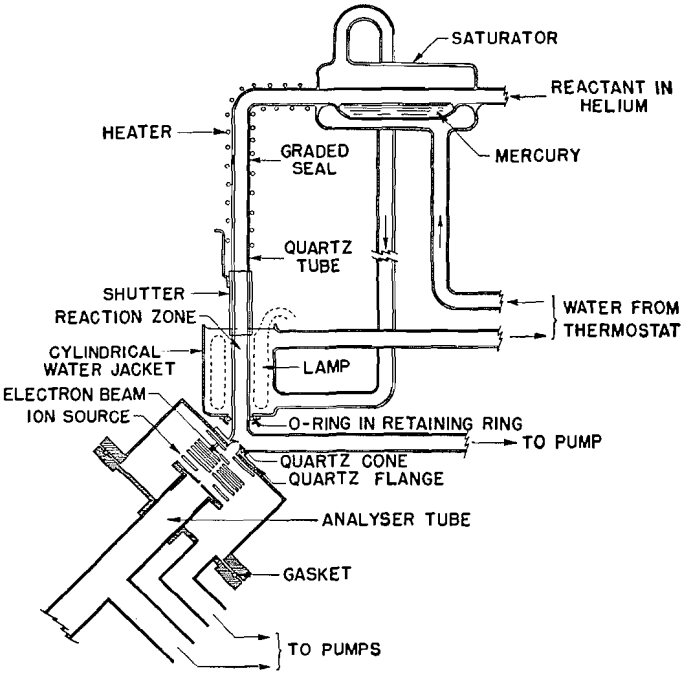

FIG. 1. The reaction system.

reactant gas, at a partial pressure of a few microns, was carried in a stream of helium at about 8 mm. pressure through the mercury saturator into the reaction zone. Just beyond the reaction zone the gas stream passed over a quartz cone containing a small orifice opening into the ionization chamber of a mass spectrometer. A suitable rate of flow was obtained by a pump of large capacity.

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The reactor itself was constructed of a length of quartz tubing of 7 mm. inside diameter bent into a right angle. At the elbow thus formed a larger tube of quartz, suitably drawn down, was sealed. This tube was cut off and flared out to form a flange with a central hole, into which was sealed a quartz cone of the type described previously (21). The tip of this cone, which had been pierced by a spark to form a circular hole 28μ in diameter, projected about 2 mm. into the reactor tubing. By means of the flange, the reactor was cemented to the top of the vacuum jacket of the mass spectrometer tube with Apiezon W wax. This seal was sufficiently soft to prevent breakage of the quartz by differential expansion. A copper cooling coil (not shown in Fig. 1) soldered to the top of the vacuum jacket prevented the wax from becoming too soft during outgassing of the tube, or as a result of heating by the mercury lamp.

The Mercury Lamp

Since a high intensity of unreversed 2537 Å radiation was required to produce sufficient decomposition of reactant in a contact time of a millisecond, special consideration was given to the design of the low pressure mercury lamp. A number of designs, consisting of helices of quartz of various internal diameters, were tried, but all were inferior to the design shown in Fig. 2.

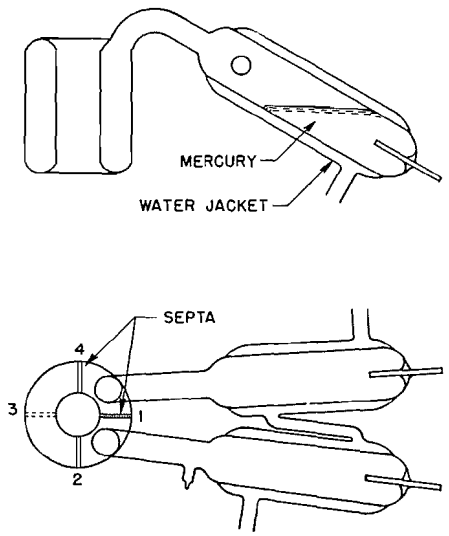

FIG. 2. The mercury lamp.

The body of the lamp consisted of two concentric cylinders of quartz tubing with internal diameters of 13 mm. and 23 mm. These were sealed together at the top and bottom to form an annular cell 36 mm. long. Four longitudinal septa were provided as shown in Fig. 2, the septa numbered 2 and 4 having a space at the bottom and that numbered 3 having a space at the top. Septum No. 1 extended the full length of the cell. The discharge was in this way forced to proceed in a zigzag path which filled the cell almost completely. The electrodes were water-cooled mercury pools. After being thoroughly

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outgassed by heating, the lamp was filled with neon at a pressure of 1.5 mm. When operated from a source of 220 v. d-c. through a series resistor the lamp was started by being touched with a Tesla coil. At a current of 4–5 amp. the voltage drop across the lamp was 90 v. To prevent self-reversal the body of the lamp and the electrodes required water cooling. Conditions for the maximum output of unreversed 2537 Å radiation could be rapidly determined by observing the extent of decomposition of ethylene flowing through the reactor. The maximum output was found to occur with the electrodes at about 10°C. and the body of the lamp at 55–60°C. It was found, rather surprisingly, that the partial pressure of mercury in the lamp was not determined by the temperature of the mercury pool electrodes. Even with the electrodes at 10°C. and the body of the lamp at 60°C., mercury slowly condensed in the latter. Evidently the pumping action of the current was able to overcome the rate of diffusion. It is interesting to note that the temperature of optimum output agrees quite well with that of 50°C. found for a low pressure lamp with iron electrodes (14) although the criterion for maximum output was not the same. In the present work only the unreversed 2537 Å line was effective, while in the work of Heidt and Boyles the output was measured by uranyl oxalate actinometry, which would respond to the wings of the line as well.

The vapor pressure of mercury at 60°C. is 25.2μ and with this partial pressure in the reactor the absorption of the 2537 Å line was probably complete in the 7 mm. diameter of the reactor tube. Owing to the rapid deposit of polymeric layers on the reactor at high reactant pressures it was not possible to measure the amount of ethylene decomposed under conditions of complete quenching. It was found, however, that a quantity of ethylene greater than that equivalent to 1.39 cc. (the illuminated volume) at 0.010 mm. could be decomposed in 0.001 sec., i.e. about 5×10^{17} molecules/sec. It is probable that the output of unreversed 2537 Å radiation falling on the reaction volume of 1.39 cc. was in excess of 10^{18} photons/sec., an amount roughly the same as that found by Heidt and Boyles.

The Water Circulating System

The arrangement shown in Fig. 1 for maintaining the body of the lamp and the reactor at 60°C. was found to be convenient. A cylindrical Pyrex water jacket was made with a hole in the bottom slightly larger than the outside diameter of the reactor tubing. A Pyrex retaining ring cemented over the hole served to hold a rubber O-ring, making a watertight seal around the reactor tube. This allowed the lamp and water jacket to be slid upward along the reactor tube so that the reactor could be cleaned by heating with a torch when polymeric deposits in the reactor reduced the transparency. Flowing oxygen through the reactor while flaming removed the most stubborn deposits.

Water connections to the mercury saturator and the thermostat were made by means of ball and socket ground joints which could be removed to allow the water jacket to be moved. It was found that contact of the cooling water with metal parts caused an opaque deposit to be formed on the lamp. Consequently distilled water was used, and the thermostat and connecting tubing

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were also made of glass. A glass centrifugal pump provided sufficient pressure to pump water through the jacket of the mercury saturator to the water jacket. The overflow from the latter returned to the thermostat. When the lamp was operating, the temperature of the reactor was a degree or so higher than that of the saturator. This served to prevent condensation of mercury in the reactor.

The Gas Flow System

The control of the helium flow and the addition of reactants at a constant proportion was the same as that described previously (20). Using a mechanical pump with a free air capacity of 140 liters/min., a flow through the reactor of 50–60 meters/sec. could be obtained with helium pressures of from 7 to 13 mm. The rate of flow was adjusted over the range of 10–60 meters/sec. by means of taps of various size in the pumping lead.

The Mass Spectrometer and Operation

The mass spectrometer has been described in earlier papers of this series (21, 20). The identification of the free radicals was done by the low electron energy method of Eltenton (7). In some cases the long periods of illumination required for the complete scanning of spectra at 50 v. resulted in the formation of sufficient polymer in the reactor to change the fraction of reactant decomposed during the time of scanning. This frequently interfered with the measurement of the spectra of the reaction products.

It has been assumed throughout this work that the appearance of a given ion at an electron energy appreciably less than that required to produce the ion from any identifiable stable compound present indicated the presence of a free radical with this mass. Where possible the identification was supplemented by a search for the corresponding dimerization product. It is, of course, possible that the appearance potential of a given ion from an excited molecule such as $C_3H_6^*$ or $C_4H_8^*$ might be lower than the normal appearance potential. It seems reasonable to suppose that in such an excited molecule the appearance potentials of all ions would be lowered by a similar amount. If this were detectable by the present apparatus it would lead to the spurious detection of "free radicals" of a mass number corresponding to each ionic species formed by electron impact on the excited molecule. No such effect was found in the present apparatus. The lifetimes of such excited molecules are short compared to those of free radicals, and an insignificant fraction would survive long enough to be struck by an electron.

Detection of H Atoms

A difficulty arose in the detection of hydrogen atoms produced in some of the reactions studied. In experiments in which hydrogen was reacted with Hg ($^3P_1$) atoms, the amount of reaction was much less than expected, H atoms being detected only in small amounts. It was concluded that the combination of H atoms to H_2 occurred rapidly, most probably on the walls of the ionization chamber. Consequently, a failure to detect H atoms among the products of decomposition of a compound was not a proof that they were not formed. On the other hand the formation of H_2 by reactions such as

$$H + RH \rightarrow H_2 + R \qquad [15]$$

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is undoubtedly too slow at 60°C. to form appreciable quantities of H_2 under the reaction conditions used. In earlier work with CH_3 radicals (15) it was found that even at 850°C. a small amount of methane found among the products of decomposition of mercury dimethyl did not arise from reactions such as

$$CH_3 + RH \rightarrow CH_4 + R \qquad [16]$$

but rather from reactions in the ion source. For this reason the formation of H_2 by reaction [15] at 60°C. was considered to be negligible.

Contact Times

In almost all the experiments described a standard pressure of helium of 7.8 mm. was used. The contact time was varied either by changing the pumping speed, or more conveniently by reducing the length of the illuminated zone by a cylindrical shutter of tantalum (Fig. 1).

RESULTS AND DISCUSSION

Ethylene

In the photosensitized decomposition of ethylene the only products of any importance were acetylene and hydrogen. No other products were found in the mass range 2–100 except for small peaks (~0.5% of C_2H_2 peaks) at mass 52 and 50. No radicals could be detected at mass 27 and no butadiene was formed. The extent of decomposition and the yields of hydrogen and acetylene for a typical experiment are given in Table I. The carbon balance has an

TABLE I

PHOTOSENSITIZED DECOMPOSITION OF ETHYLENE

C_2H_4 pressure (μ)		C_2H_4 reacted		Contact time	C_2H_2 found		H_2 found	
Lamp off	Lamp on	μ	%	(millisec.)	μ	Yield (%)	μ	Yield (%)
3.03	1.78	1.25	41.3	1.4	1.27	102	1.06	85

estimated error of 5% and the hydrogen balance is considerably more uncertain. It may be concluded that vinyl radical production, if it occurred, amounted to less than 3% of the total reaction. Experiments with higher pressures of ethylene also showed no sign of vinyl radical production. In a separate experiment in which acetylene was irradiated it was found to decompose hardly at all in the same contact time, so that no secondary reactions would be expected. These results constitute good evidence for a molecular process for the decomposition of ethylene at 60°C., and are in agreement with the recent experiments of Cvetanović and Callear (2, 4) in this respect.

Propylene

Under the same experimental conditions as with ethylene, the decomposition of propylene led to the formation of allyl radicals in considerable amounts as shown by a search at low electron energies. The dimer of allyl, 1,5-hexadiene, was also produced. Other products were allene in appreciable quantity, and traces of ethylene and acetylene. Since the mass spectrum of the allyl radical

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in the mass 40 range was not determined, a quantitative measurement of the amount of allene could not be made and a carbon balance was not obtained. The extent of decomposition and the yield of hydrogen (presumably from H atom combination) are shown in Table II. It was possible to show in the following way that allene was produced mainly by a secondary reaction. At an electron energy of about 10 v., the mass 40 (allene) and 41 (allyl) peaks were free from contributions from other compounds and the ratio of their heights was proportional (but not equal) to the ratio of allene and allyl present. As the contact time was shortened by using the shutter, it was observed that the amount of allene decreased greatly while the amount of allyl decreased only slightly (Table II). A large decrease in allene production

TABLE II

PHOTOSENSITIZED DECOMPOSITION OF PROPYLENE

C_3H_6 pressure (μ)		C_3H_6 reacted		Contact time	H_2 found		Mass	Mass	Ratio
Lamp off	Lamp on	μ	%	(millisec.)	μ	Yield (%)	40	41	40/41
1.40	1.16	0.24	17.1	1.4	0.21	88	—	—	—
1.36	1.22	0.14	10.3	0.7	0.11	79	—	—	—
Low electron energy experiments				0.7	—	—	0.40	0.70	0.57
				0.4	—	—	0.10	0.62	0.16
				0.2	—	—	0.05	0.55	0.09

would be expected if it were produced from allyl by a secondary process, but not if it were produced in a primary molecular split of propylene. The relatively small decrease in the amount of allyl shows that the decrease in production resulting from the shorter contact time was nearly balanced by the decrease in reactions removing allyl. The high yield of hydrogen (Table II) indicates that the fate of most of the allyl radicals was to give a hydrogen atom. This also supports the view that allyl radicals were disappearing rapidly to form allene and an H atom. Three reactions by which this could occur may be considered:

$$CH_2{:}CH{\cdot}\dot{C}H_2 + H \rightarrow CH_2{:}C{:}CH_2 + H_2 \quad [17]$$

$$CH_2{:}CH{\cdot}\dot{C}H_2{}^* \rightarrow CH_2{:}C{:}CH_2 + H \quad [18]$$

$$CH_2{:}CH{\cdot}\dot{C}H_2 + Hg(^3P_1) \rightarrow CH_2{:}C{:}CH_2 + H + Hg(^1S_0). \quad [19]$$
$$\text{(or HgH)}$$

Reaction [17] is undoubtedly too slow at 60°C. to be effective. Such abstraction reactions are several orders of magnitude slower than dimerizations, and only a small proportion of allyl radicals had time to dimerize. The second reaction is improbable on energetic grounds. Of the 112 kcal. imparted by a $Hg(^3P_1)$ atom, about 77 kcal. (27) are required to break the $CH_2{:}CH{\cdot}CH_2$–H bond. The allyl radicals could have a maximum excitational energy of 35 kcal., neglecting the translational energy imparted to the H atom. From the heat of formation of allene, 45.9 kcal./mole at 25°C. (25), and of allyl, 32 kcal./mole (22), a dissociation energy of 65 kcal./mole can be derived for the C_3H_4–H bond in allyl. Even if this value were in error by more than a few kilocalories there is not sufficient energy available for a "hot" allyl to dissociate.

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The third possibility, reaction [19], is generally not considered in conventional photosensitized reaction experiments because of the relatively low concentrations of radicals and excited mercury atoms. In the present work, however, the high intensity of radiation and the low pressure of olefin results in relatively large concentrations of radicals and excited mercury atoms, and collisions between these are not statistically negligible. It should be noted from the reactions given below that if reaction [19] did not occur, the yield of H_2 would be 50%, and if all allyl radicals were removed by this reaction, the yield would be 100%. A yield of 79%, as found, indicates that some $2\times(79-50)$ or 58% of the radicals had decomposed in this way. Since propylene itself was decomposed to the extent of 10.3% in a somewhat greater contact time, it would appear, if this interpretation is correct, that allyl radicals have a cross section for reaction with $Hg(^3P_1)$ atoms about five times larger than has propylene. This could arise from a larger collision cross section for quenching or a larger quantum yield, or from a combination of both.

On this basis the following reactions would account for the products found:

$$CH_2{:}CH\cdot CH_3 + Hg(^3P_1) \rightarrow CH_2{:}CH\cdot\dot{C}H_2 + H + Hg(^1S_0) \quad [20]$$

$$CH_2{:}CH\cdot\dot{C}H_2 + Hg(^3P_1) \rightarrow CH_2{:}C{:}CH_2 + H + Hg(^1S_0) \quad [19]$$

$$2CH_2{:}CH\cdot\dot{C}H_2 \rightarrow \text{1,5-hexadiene} \quad [21]$$

$$H + H + M \rightarrow H_2 + M. \quad [22]$$

The present work gives no direct indication as to whether reactions [20] and [19] proceed by formation of HgH or by excited molecule formation. As mentioned above, a large part of reaction [22] must proceed in the ion source.

Isobutene

The extent of decomposition of isobutene under the same experimental conditions as used with propylene and ethylene is given in Table III, along

TABLE III

PHOTOSENSITIZED DECOMPOSITION OF ISOBUTENE

Isobutene pressure (μ)		Isobutene decomposed		Contact time (millisec.)	H_2 found	
Lamp off	Lamp on	μ	%		μ	Yield (%)
1.75	1.57	0.18	10.4	1.4	0.10_1	56.0
1.72	1.61	0.11	6.5	0.7	0.05_6	50.0

with the yield of H_2 based on the isobutene decomposed. A search for radicals at low electron energy showed that a radical of mass 55 was produced in considerable amounts, and that methyl radicals were present in small amounts. Allene, an octadiene, and a pentene were also produced. The spectrum of the octadiene was similar to that of 2,5-dimethyl-1,5-hexadiene, the dimer of the β-methallyl radical (22). Of the two possible radicals of mass 55 which could be formed from isobutene

$$\dot{C}H{:}C\cdot CH_3 \quad \text{and} \quad CH_2{:}C\cdot\dot{C}H_2$$
$$\dot{C}H_3 \qquad\qquad\qquad\quad \dot{C}H_3$$

the second (β-methallyl) is capable of resonance stabilization because of its allylic structure, and the β-methallyl–H bond is correspondingly weak, 76 ± 3 kcal./mole (22). From this consideration and from the identity of the dimer, it is almost certain that the radical formed is β-methallyl. Considering the structure of isobutene, neither methyl radicals nor allene appear to be likely products of a primary split. They have, however, been identified as the products of thermal decomposition of β-methallyl radicals (22). In view of this it is reasonable to believe that they arise from the reaction of a β-methallyl radical with a $Hg(^3P_1)$ atom, in a manner analogous to reaction [19]. As with propylene, the decomposition of a radical carrying excitation energy left over from the primary split is unlikely on energetic grounds. From the heat of formation of allene, 45.9 kcal./mole (25), and that of β-methallyl radical, 21.3 ± 3 kcal./mole (22), and methyl radical, 32.6 kcal./mole (13), the dissociation energy of the C_3H_4–CH_3 bond in β-methallyl radical is 57 kcal./mole. From ΔH_f(isobutene) $= -3.3$ kcal./mole (25) and ΔH_f(β-methallyl) as above, D(β-methallyl–H) $= 76$ kcal./mole. Consequently the maximum excitation of a "hot" β-methallyl would be only 36 kcal.

The reactions which would account for the products found are then:

$$CH_2{:}C(CH_3)CH_3 + Hg(^3P_1) \rightarrow CH_2{:}C(CH_3)\dot{C}H_2 + H + Hg(^1S_0) \quad [23]$$

$$CH_2{:}C(CH_3)\dot{C}H_2 + Hg(^3P_1) \rightarrow CH_2{:}C{:}CH_2 + CH_3 + Hg(^1S_0) \quad [24]$$

$$2CH_2{:}C(CH_3)\dot{C}H_2 \rightarrow \text{2,5-dimethyl-1,5-hexadiene} \quad [25]$$

$$CH_3 + CH_2{:}C(CH_3)\dot{C}H_2 \rightarrow C_5H_{10} \quad [26]$$

$$H + H + M \rightarrow H_2 + M. \quad [22]$$

These reactions would lead to a yield of H_2 of 50%, in good agreement with that found (Table III). In addition to these products small amounts of propylene and a substance of mass 54 were found. It is difficult to understand how either of these products could be produced either as a primary reaction or by secondary reactions among the species identified. The formation of butadiene (mass 54) appears improbable since an extensive rearrangement would be required. One possible origin of a substance of mass 54 would be the removal of a hydrogen from β-methallyl to form methylene cyclopropane:

$$CH_2{:}\underset{\displaystyle CH_3}{\overset{|}{C}}\!-\!\dot{C}H_2 + Hg(^3P_1) \rightarrow CH_2{:}C\!<\!\begin{matrix}CH_2\\ CH_2\end{matrix} + H + Hg(^1S_0). \quad [27]$$

The preparation of methylene cyclopropane has been carried out (9) by removal of chlorine as follows:

$$CH_2{:}\underset{\displaystyle CH_2Cl}{\overset{|}{C}}\!-\!CH_2Cl \xrightarrow{Mg} CH_2{:}C\!<\!\begin{matrix}CH_2\\ CH_2\end{matrix} \quad [28]$$

This reaction is essentially similar to reaction [27].

The primary split, reaction [23], is the same as that suggested by previous workers (11) although the final products of the reaction are quite different.

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The products also differ from those found by Allen and Gunning (1). This is to be expected in view of the great difference in the isobutene pressure in the two experiments. The latter authors found evidence for excited molecule formation and it is probable that reaction [23] proceeds by this means. The dimer found by these authors may have been at least partly 2,5-dimethyl-1,5-hexadiene rather than a dimer of isobutene as they suggested.

2-Butene

In the photosensitized decomposition of 2-butene, a radical of mass 55, presumably the γ-methallyl radical $CH_3 \cdot CH{:}CH \cdot \dot{C}H_2$, was produced in considerable amounts. Other products were butadiene, hydrogen, some propylene, and possibly some allene. A dimer was also produced, whose spectrum was similar to the spectrum of 2,6-octadiene produced from γ-methallyl radicals previously (22). As no pure sample of 2,6-octadiene was available,

TABLE IV

PHOTOSENSITIZED DECOMPOSITION OF 2-BUTENE

2-Butene pressure (μ)		2-Butene decomposed		Contact time	H_2 found		Mass 54	Mass 55	Ratio
Lamp off	Lamp on	μ	%	(millisec.)	μ	Yield (%)	(low *E*)	(low *E*)	54/55
1.68	1.48	0.20	11.9	1.4	0.17	85.0	1.9	1.10	1.70
1.68	1.59	0.11	6.5	0.7	0.09_2	83.6	1.0	0.90	1.10

this identification was not completely certain. In order to establish whether butadiene was a primary product, the ratio of the 54 to 55 peaks at low electron energy was examined at different contact times. The ratio decreased but not as greatly as in the similar experiments with propylene. There is a possibility that some butadiene may be formed from 2-butene by a molecular process as well as by the decomposition of γ-methallyl radicals. As in the case of isobutene, the further decomposition of a "hot" radical can be ruled out. The dissociation energy of the γ-methallyl–H bond has been given as 80±3 kcal./mole (22) and the maximum excitation of the radical could be 32 kcal. From ΔH_f(butadiene) = 26.3 kcal./mole (25) and ΔH_f(γ-methallyl radical) = 26±3 kcal./mole (22), the butadiene–H bond in γ-methallyl radical would be 52 kcal./mole. Insufficient energy would be available for a "hot" radical to decompose spontaneously.

1-Butene

The extent of decomposition of 1-butene and the yield of hydrogen are shown for two contact times in Table V. A search at low electron energy showed that allyl and methyl radicals were present in abundance and a radical of mass 55 in moderate amounts. Other products were allene, 1,5-hexadiene, ethane, hydrogen, and small amounts of pentene, butadiene, and propylene. With higher pressures peaks at mass 91, 95, and 96 appeared, suggesting the presence of a heptadiene. Experiments using the shutter indicated that allyl,

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TABLE V

PHOTOSENSITIZED DECOMPOSITION OF 1-BUTENE

1-Butene pressure (μ)		1-Butene decomposed		Contact time (millisec.)	H_2 found	
Lamp off	Lamp on	μ	%		μ	Yield (%)
2.42	1.87	0.55	22.7	1.4	0.17	31
2.43	2.08	0.35	14.4	0.7	0.10	29

methyl, and the radical of mass 55 were primary products. The latter was undoubtedly a methallyl radical, the two forms $CH_2{:}CH\cdot\dot{C}H\cdot CH_3$ (α) and $\dot{C}H_2\cdot CH{:}CH\cdot CH_3$ (γ) being resonance hybrids.

The spectra given in Fig. 3 illustrate the detection of the allyl and methallyl radicals formed from 1-butene. Fig. 3A shows a portion of the low electron energy spectrum of 1-butene with the lamp off. With the lamp on and the shutter completely withdrawn (Fig. 3B) the increase in the mass 40, 41, and 42 peaks shows the presence of allene, allyl, and propylene. With the shutter halfway in, as in Fig. 3C, the contact time was halved, and the propylene and allene peaks were greatly reduced, while the allyl peak remained almost unchanged. This shows that allene and propylene were products of secondary reactions. In Fig. 3D the spectrum was obtained at an electron energy low enough to avoid the formation of the $C_4H_7^+$ ion (mass 55) by electron impact. With the lamp on (Fig. 3E) and the shutter withdrawn, the increase in the mass 54 and 55 peaks indicates the presence of butadiene and methallyl radicals. With the shutter halfway in (Fig. 3F), the butadiene peak was considerably reduced, while the methallyl peak was only slightly changed. Fig. 3G shows the 50 v. spectrum of the dimers 1,5-hexadiene at mass 82, 81, and 67; pentene at mass 70; and peaks at 96, 95, and 91, possibly heptadiene, barely visible.

The formation of the methyl, allyl, and methallyl radicals as primary products indicates that two modes of splitting must occur as primary steps:

$$CH_2{:}CH\cdot CH_2\cdot CH_3 + Hg(^3P_1) \rightarrow CH_2{:}CH\cdot\dot{C}H_2 + CH_3 + Hg(^1S_0) \quad [29]$$

$$CH_2{:}CH\cdot CH_2\cdot CH_3 + Hg(^3P_1) \rightarrow CH_2{:}CH\cdot\dot{C}H\cdot CH_3 + H + Hg(^1S_0). \quad [30]$$

The other products can be accounted for by the following reactions:

$$CH_2{:}CH\cdot\dot{C}H_2 + Hg(^3P_1) \rightarrow CH_2{:}C{:}CH_2 + H + Hg(^1S_0) \quad [31]$$

$$CH_2{:}CH\cdot\dot{C}H\cdot CH_3 + Hg(^3P_1) \rightarrow CH_2{:}CH\cdot CH{:}CH_2 + H + Hg(^1S_0) \quad [32]$$

$$2CH_3 \rightarrow C_2H_6 \quad [33]$$

$$2CH_2{:}CH\cdot\dot{C}H_2 \rightarrow \text{1,5-hexadiene} \quad [34]$$

$$CH_3 + CH_2{:}CH\cdot\dot{C}H\cdot CH_3 \rightarrow \text{pentene} \quad [35]$$

$$CH_2{:}CH\cdot CH_2 + CH_2{:}CH\cdot\dot{C}H\cdot CH_3 \rightarrow \text{heptadiene} \quad [36]$$

$$CH_2{:}CH\cdot\dot{C}H_2 + H \rightarrow \text{propylene} \quad [37]$$

$$H + H + M \rightarrow H_2 + M. \quad [22]$$

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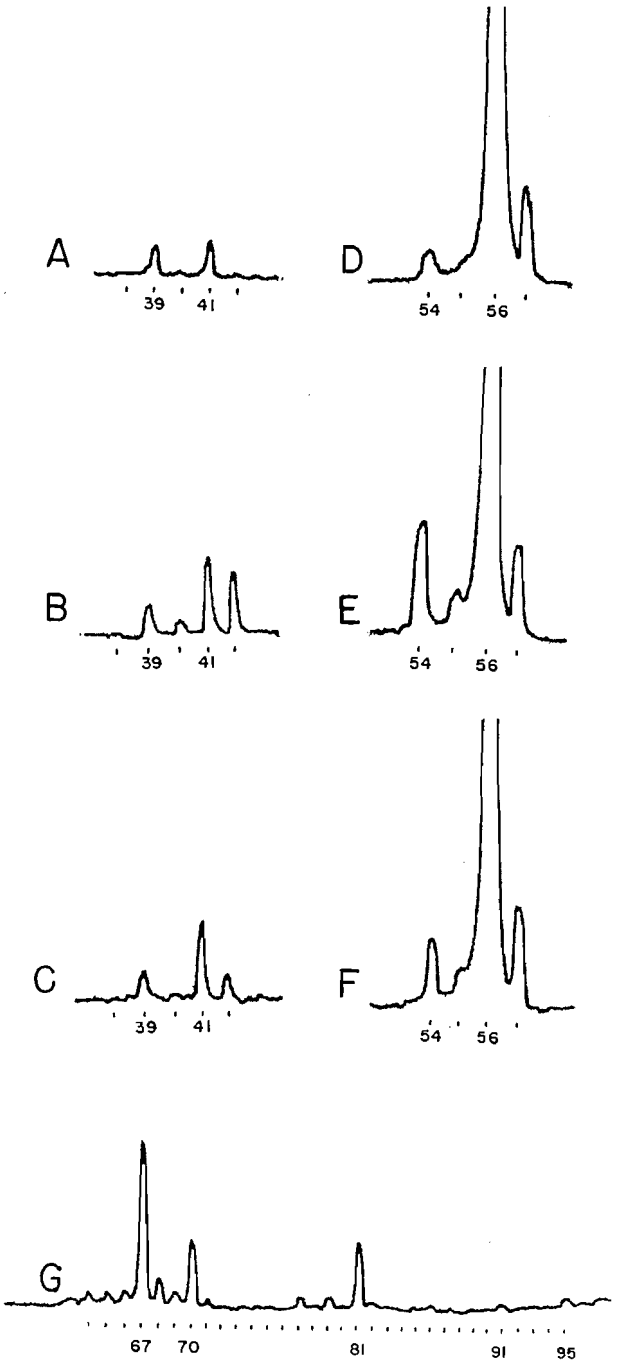

FIG. 3. Portions of mass spectra illustrating the detection of allyl and methallyl radicals in the decomposition of 1-butene. As described in the section on 1-butene, the propylene and butadiene are formed as secondary products.

It is interesting to compare the energies required for the two primary steps given above. From ΔH_f(allyl) = 32 kcal./mole (22), $\Delta H_f(CH_3)$ = 32.6 kcal./mole (13), ΔH_f(γ-methallyl) = 26 kcal./mole (22), ΔH_f(1-butene) = 0.280 kcal./mole (25), and ΔH_f(H) = 51.5 kcal./mole, the following bond dissociation energies can be derived:

$$D(\text{allyl–}CH_3) = 64 \text{ kcal./mole},$$

$$D(\text{methallyl–H}) = 77 \text{ kcal./mole}.$$

If the decomposition of 1-butene proceeds, as seems probable, by the formation of an excited molecule (26), then this molecule would suffer bond rupture after the time interval required for sufficient vibrational energy to become associated with a particular bond. Although the C–H bond is stronger than the C–C, the difference is only about 13 kcal., and it is not surprising that a molecule with 112 kcal. of excitation energy should be able to decompose by either mode. It is not possible from the present data to establish the relative probabilities of reactions [29] and [30], but the greater abundance of the ethane and hexadiene over the pentene and heptadiene, as well as the relative size of the radical peaks, indicates that the C–C split predominates. The low yield of H_2 compared with that found for propylene and 2-butene is also consistent with a smaller probability for the C–H split. The proportion of H_2 found is not much greater than was estimated above to result from the reaction of excited mercury atoms with the allyl radicals from propylene.

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RADIOIODINE EXCHANGE BETWEEN IODOSTEARIC ACID MONOLAYERS AND SUBSTRATE IODIDE[1]

By R. F. Robertson, C. A. Winkler, and S. G. Mason

ABSTRACT

Velocities of exchange of iodine between monolayers at the air/water interface of α-iodostearic acid and potassium iodide in the substrate have been measured over a range of monolayer and substrate concentrations and temperatures using a radioactive tracer technique. The pressure–area isotherms were also determined. The process was followed by measuring the decrease in counting rate immediately above the surface. It is shown theoretically that ions released to the substrate diffuse rapidly and do not contribute appreciably to the counting rate. The velocity of exchange was found to be first order in concentration of the surface phase and of higher but indeterminate order in concentration of potassium iodide. In the region of 18°C., where a transition from liquid-condensed to liquid-expanded film occurs, the reaction velocity constant undergoes a discontinuous increase. Activation energies of 8.0 and 10.8 kcal./mole were found for exchange in the condensed and expanded films respectively.

INTRODUCTION

The kinetics of chemical reactions occurring in monolayers at air/water interfaces have been studied by following changes in the surface potential (22), or in the area per molecule at constant pressure in the film (5). The reactions studied thus far have been limited to oxidation (4, 18, 22, 26), hydrolysis (5, 3, 16, 6, 27, 13, 28), and lactonization processes (12, 24). Both experimental methods involve indirect measurement of the changes in concentration of the reactants in the surface films from which the reaction velocity is computed. A more direct method of following such reactions is to use monolayers containing radioactively tagged groups which on reaction pass into the substrate. Such a method could also be used to study exchange reactions between films and substrates.

Tracer techniques have already been used in the study of soluble films (14). Carbon-14 tagged films deposited by the method of Blodgett (9) on various surfaces have been used to measure backscattering and chemical reactions in adsorbed films (7), to investigate lubrication problems (10), and to study surface diffusion phenomena (15). Deposited radioactive monolayers have been proposed as standard β-ray sources because of their stability and ease of reproduction and negligible self-absorption (8).

To the present, however, no investigations of insoluble monolayers at the air/water interfaces have been reported in which the tracer technique has been employed. In this paper a successful application of the method to the study of halogen exchange between a tagged monolayer molecule and a reactant in the substrate is described. Results are presented for iodine-exchange between monolayers of α-iodostearic acid and potassium iodide substrates at various surface and substrate concentrations over a range of temperatures.

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EXPERIMENTAL PART

Materials

Radioiodine was incorporated by an exchange reaction into α-iodostearic acid which was prepared from the corresponding bromo acid. Iodine-131 was selected as the tracer element because it is a β-emitter of intermediate energy (0.6 Mev.), has a convenient half life (8.0 days), and is readily available in carrier-free form.

α-Bromostearic Acid

This acid, prepared from purified stearic acid by the method of Hell and Sadomsky (21), was recrystallized 10 times from petroleum ether (40°–60°C. boiling range) and three additional times from 95% ethanol at −13°C. The pure α-bromostearic acid crystallized as white needles and plates. Melting point 60.1–60.5°C. (Hell and Sadomsky 60°C.).

α-Iodostearic Acid

This acid was prepared essentially by the method of Frewing (17). α-Bromostearic acid (0.058 mole) was refluxed with KI (0.116 mole) in 300 ml. of 95% ethanol for three hours. The ethanol was then removed *in vacuo* and the α-iodostearic acid dissolved in hot benzene. After eight recrystallizations at +8°C. from benzene, the acid was recrystallized three additional times from 95% ethanol at −13°C. The crystals were similar in appearance to those of the α-bromostearic acid. Melting point 67.0–67.3°C. (Frewing 67°C.).

Radioactively Tagged α-Iodostearic Acid

The exchange was carried out in a 250 ml. erlenmeyer flask with a rounded bottom. One ground-glass joint was attached to the neck of the flask, and a second to the side just above the rounded bottom.

Ten millicuries of aqueous carrier-free and buffered NaI^{131} solution (AECL grade) was placed in the flask and the water removed by freeze-drying. A weighed sample of 0.01 to 0.02 gm. of inactive α-iodostearic acid was dissolved in 4 ml. of 95% ethanol and added to the reaction flask over the freeze-dried residue (largely buffer). The resulting solution was gently refluxed for two to three hours to allow the exchange reaction to occur, and then allowed to cool to room temperature.

A sintered-glass filter tube was inserted in place of the stopper in the ground-glass joint on the side, the flask was tipped until the filter was elevated somewhat above the body of the flask, and 200 ml. of 1 *N* HCl solution was added. An emulsion of fatty acid in HCl solution formed initially, but after the flask had been left for two to three hours or sometimes overnight, fairly large aggregates of fatty acid appeared. The aqueous layer was then filtered off, the fatty acid being retained on the flask walls and on the filter. Two consecutive 50 ml. portions of 0.1 *N* HCl were then added to the flask and the precipitate of fatty acid washed as completely as possible on to the filter where it was again washed twice with 25 ml. portions of distilled water. The flask was again connected to the freeze-drying apparatus and the water completely removed from the flask and filter tube.

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The dry I^{131} α-iodostearic acid on the sides of the flask and on the filter was dissolved by washing with warm benzene. The resulting solution was then made up to volume with benzene in a 25 ml. volumetric flask. The benzene solution of I^{131} α-iodostearic acid was stored in the stoppered volumetric flask away from light, behind a lead shield. The concentration of α-iodostearic acid in the benzene solution was determined, when necessary, from the measured pressure–area relation of a known volume of the fatty acid solution, spread to form a monolayer.

The relative quantities of NaI^{131} and α-iodostearic acid used in the above preparations were chosen by calculation to give an experimentally convenient initial radioactive counting rate of about 5000 counts per cm.^{2} per min. when the acid is spread on a surface area of about 40 Å^2 per molecule. In the calculation it was assumed that 50% exchange represented complete reaction and that the over-all counting efficiency was 50%. The counting rates found experimentally were surprisingly close to the expected values.

Other Materials

All the materials used in the experiments and preparations, including the paraffin used in coating the monolayer trough, were purified to ensure the absence of surface-active contaminants. Routine checks were made by spreading pressure measurements in the conventional way.

Apparatus

The general arrangement of the monolayer trough and accessory equipment is shown in Fig. 1. The stainless steel trough (carefully coated with paraffin

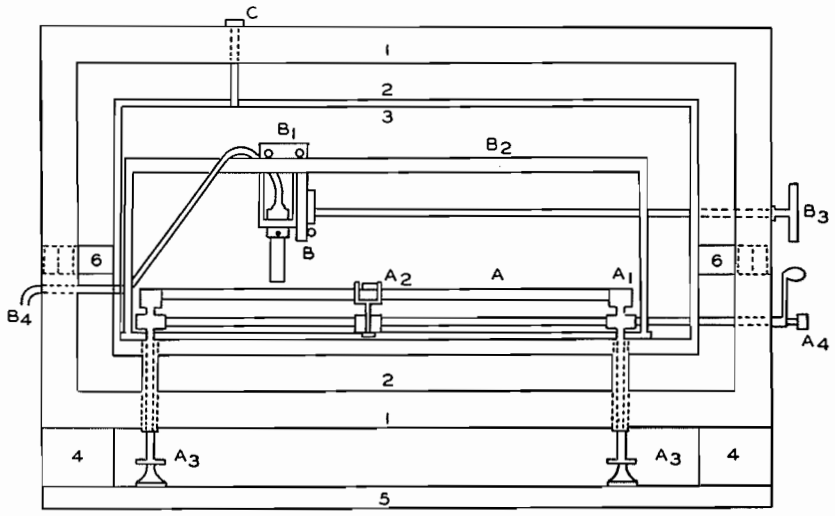

FIG. 1. Monolayer trough arrangement (schematic).

Air bath: 1, insulation; 2, chamber containing copper coils; 3, air chamber; 4, cork supports; 5, stone pedestal; 6, windows (triple glass).

Film trough: A, trough; A_1, trough support; A_2, barrier moving device; A_3, adjustable feet; A_4, barrier moving device.

Geiger tube assembly: B, Geiger tube; B_1, tube carriage; B_2, tracks for carriage; B_3, handle tube carriage; B_4, shielded lead to rate meter.

Surface balance: C, sleeve for wire of surface balance.

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before use) was enclosed in an air bath, the temperature of which was held constant by pumping water from external thermostats (not shown) through copper coils in the air bath. The water in the trough was also held to constant temperature by circulation of water from the thermostats. The temperature of the solution in the trough could be controlled manually to within ±0.2°C. of the temperature of the air bath. A reservoir of water, into which filter paper hung and which was similarly held at constant temperature, maintained a saturated atmosphere within the air bath. After temperature equilibration the temperature of the air bath could be held within ±0.1°C. for periods of 15 hr. in the range of 10°C. to 40°C.

The surface balance was the Harkins vertical pull type (20). An image of a hairline was reflected from a small mirror mounted at the main knife edge of the balance, and projected on a curved scale. The balance had a sensitivity of 0.48 dyne per cm. per scale division of the optical lever.

The barrier of the trough could be operated by remote control from outside the box and its position in the trough could be determined from the reading on an externally mounted revolution counter. The Geiger tube mounting was also remote-control-operated from outside the box. The Geiger tube, which had an effective window area of 2 cm.^{2}, could be moved to scan any region of the film surface when the tube was fixed in its carrier.

The counting equipment consisted of an Electronics Associates type 1725 Ratemeter used in conjunction with an Esterline-Angus 10 milliamp. recording milliammeter. The counting rate could be recorded as a function of time on the chart of the milliammeter. The Geiger tube was a mica end-window counter (Nuclear Instrument Corp. type D 34). The fused mica/glass seal eliminated tube failures experienced with cemented mica-end-window tubes in the saturated atmosphere.

Experimental Procedure

All substrates used in the present work were allowed to come to constant temperature overnight. The technique used to obtain the pressure–area isotherms was essentially that of Adam (2). The substrate was 0.01 *N* HCl solution. Before the film was spread the surface was repeatedly swept by the barriers until a decrease in area to one-third of the original caused less than 0.05 dyne/cm. increase in surface pressure.

To spread a film, a measured volume of benzene solution of α-iodostearic acid was added dropwise at many points on the surface from an Agla micrometer syringe. Fifteen minutes were allowed for the evaporation of the benzene, the initial pressure was noted, and the film was compressed in steps every three to four minutes. Since the surface balance did not permit accurate measurements of decreases in surface pressure, only compression curves were obtained.

The same spreading technique was used in the exchange experiments except that the Agla syringe was replaced with a microliter syringe-pipette. Sufficient acid was added to the surface during spreading to bring the surface pressure to a value just below that desired for the exchange experiment. The final pressure adjustment was made by compression of the film.

The slide of the surface balance was removed after each pressure measurement during an exchange reaction to prevent undue contamination with substrate solution and film molecules, and was cleaned between each measurement. At the end of an exchange experiment the active film was removed by suction through a capillary pipette to a suction flask.

Directly after the trough was filled with KI solution the Geiger tube was mounted in position with the end window 3 mm. above the surface to allow passage of the barrier and left inside the air bath during the period of thermal equilibration. The background counts were about 60 per min.; since the counting rates obtained with the films were of the order of 10^4 per min., no correction for background was necessary.

Standard radiochemical techniques and precautions were used at all stages of preparation and use of the radioactive fatty acid.

RESULTS

Pressure–Area Isotherms

To characterize the various types of monolayer, pressure–area isotherms were determined over 0.01 *N* HCl substrates. Because of rapid contamination

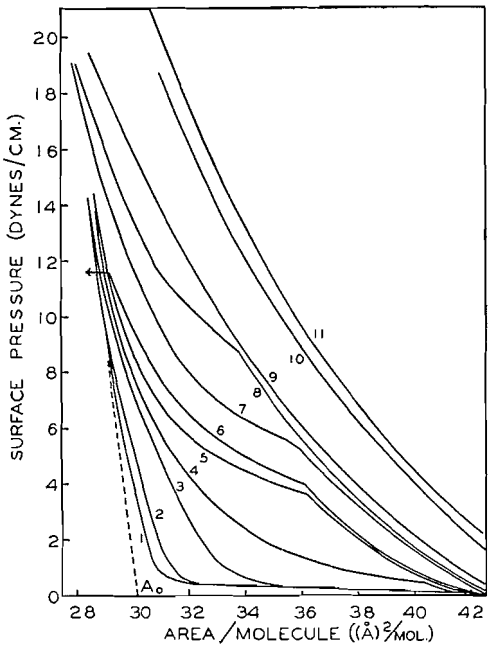

FIG. 2. Pressure–area isotherms of α-iodostearic acid.

Curve	Temp.	Curve	Temp.	Curve	Temp.
1	9°C.	5	16.4°C.	9	19.8°C.
2	10.6°C.	6	16.8°C.	10	26.4°C.
3	12.6°C.	7	17.4°C.	11	27.4°C.
4	14.8°C.	8	18.8°C.		

A_0 = area at zero compression = 30.2 Å²/molecule.

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of the slide of the surface balance when salts were present in the substrate solution, it was not possible to measure the isotherms over substrates containing potassium iodide at the relatively high concentrations used in the monolayer/substrate exchange experiments.

The isotherms between 9° and 27.4°C. are presented in Fig. 2 and are typical of fatty acids. The curves indicate the existence of three distinct types of film which may be illustrated by reference to the 17.4°C. isotherm:

1. From very low pressures up to a pressure 5.5 dynes/cm. and an area 38.95 Å^2/molecule, the film is "liquid-expanded" in the nomenclature of Adam (2). The coefficient of compressibility $K = 1/A\ (\partial A/\partial \pi)$, where π is the surface pressure and A is the area per molecule, is 2.9×10^{-2} cm./dyne, which may be compared with values of 2×10^{-2} to 7×10^{-2} cm./dyne given by Harkins (19) for this type of film.

2. Above the pressure 5.5 dynes/cm. the film is "intermediate-liquid", the initial K being 1.1×10^{-1} cm./dyne.

3. As the pressure is further increased the isotherm shows a gradual transition to a "liquid-condensed" film. At 28.45 Å^2/molecule, $K = 9\times10^{-3}$ cm./dyne.

Above 19.8°C. the films are of the liquid-expanded type. Below this temperature an intermediate-liquid film exists down to about 12°C. Between 12°C. and 19.8°C., the films are liquid-expanded at low pressures up to a transition pressure, which increases with increasing temperature, when condensation to an intermediate-liquid film occurs. As the pressure is increased the intermediate-liquid film passes gradually to the liquid-condensed film.

The isotherms yield an area at zero compression of about 30.2 Å^2/molecule. This value lies between 27.8 Å^2/molecule and 32.8 Å^2/molecule for the C_{16}–C_{17} and C_{18}–C_{21} α-bromo acids respectively (1). The marked tendency to collapse exhibited by α-iodostearic acid monolayers at temperatures below 12°C. as the surface pressure was increased above about 10 dynes/cm. made it impossible to determine the pressure–area isotherms over a large range of pressures in this condensed state. The area at zero compression may consequently be in error by as much as +1 Å^2/molecule.

Preliminary Exchange Experiments

When a monolayer of the tagged acid was deposited on a substrate containing 0.01 N HCl and potassium iodide, the counting rate decreased with time. A series of preliminary experiments showed that the rate of the process, as measured by the rate of change of counting rate, increased with increased KI concentration. From these experiments it was concluded that 1.0 M KI was the most convenient concentration for temperature coefficient measurements. Measurements at concentrations in excess of 1.5 M KI were found impractical because of crystallization of the salt on the barriers.

In the experiments, condensation of water on the end window of the Geiger tube could conceivably occur and thus cause an apparent decrease in counting rate. It was shown however that this had a negligible effect on the counting rate. In further experiments it was shown that when the film was swept off

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at any time the counting rate dropped to the normal background value of about 60 per min. so that the activity transferred from the monolayer to the substrate has a negligible influence on the background count.

The possibility that the decrease in counting rate was due to hydrolysis of the α-halogen compound to the corresponding α-hydroxy compound was investigated in a series of experiments using active films spread on 0.01 N HCl, and 0.01 N HCl substrates containing 1.0 M and 2.0 M KCl. In no case did any significant decrease in counting rate with time occur. Some films spread on 0.01 N NaOH substrates to favor hydrolysis also showed no decrease in counting rate with time.

All the foregoing experiments were made at constant total area; in all instances, including those over the KI substrates, the surface pressure remained constant, which indicated a constant chemical composition of the film. These experiments also left little doubt that the decrease in counting rate of the film on a KI substrate was associated with the presence of I^- ion in the substrate and that the observed decrease in counting rate was due to iodine exchange between the alkyl halide in the monolayer and inorganic iodide in the substrate.

Exchange Reaction

The rate of the exchange reaction was studied at various values of the surface pressure, temperature, and concentration of potassium iodide in the 0.01 N HCl substrate. The rate was computed in the following manner:

Let V moles cm.$^{-2}$ min.$^{-1}$ be the velocity (forward and reverse) of the exchange reaction

$$CH_3(CH_2)_{15}CHI^*COOH + KI \rightarrow CH_3(CH_2)_{15}CHICOOH + KI^*.$$

Let n moles/cm.^{2} be the total concentration of fatty acid in the film, and $f(t)$ be the fraction of fatty acid molecules containing radioactive atoms at time t. Assuming that the radioactive atoms are homogeneously distributed in the surface film, the rate of disappearance of radioactive atoms from the surface film is $Vf(t)$, i.e.

$$[1] \qquad -d(nf(t))/dt = Vf(t),$$

which, on integration, yields

$$[2] \qquad \log_e[f(0)/f(t)] = Vt/n.$$

If it is further assumed that the recorded counting rate $c(t)$ is proportional to $f(t)$, i.e radioactive atoms passing into the substrate do not register on the counter, Eq. [2] becomes

$$[3] \qquad \log_e[c(0)/c(t)] = kt,$$

where $k = V/n$.

Semilogarithmic plots of $c(t)$ against t in most cases yielded straight lines from which the rate constant k could be readily determined. Typical examples are illustrated in Fig. 3 for films at 25°C. and 35°C. Exceptions occurred at 18°C. as shown in Fig. 4, where the plot became linear only after approximately two hours of exchange.

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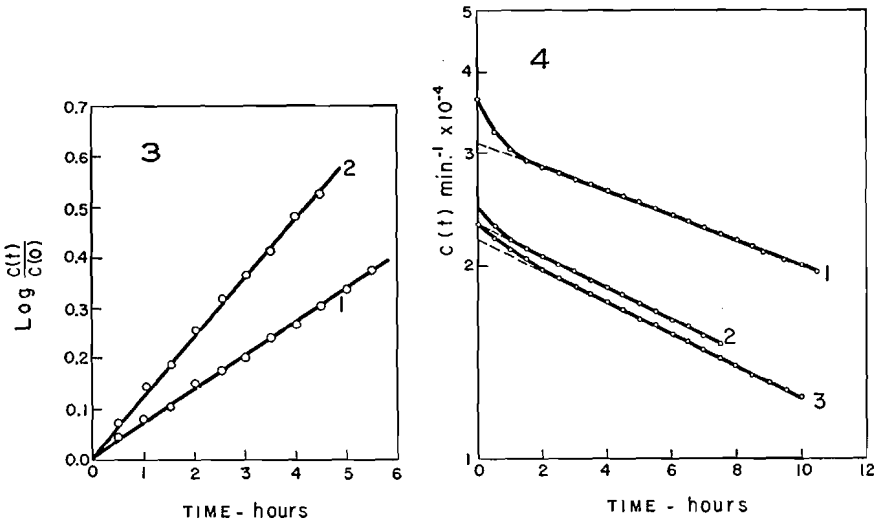

FIG. 3. Counting rate vs. time plots at 25°C., 15.5 dynes/cm. (curve 1) and 35°C., 14.6 dynes/cm. (curve 2).
FIG. 4. Semilogarithmic plots of counting rate vs. time at 18°C. at surface pressures of 14.8 dynes/cm. (curve 1) 4.3 dynes/cm. (curve 2), and 3.9 dynes/cm. (curve 3).

Values of k at various temperatures between 10°C. and 37°C. and at various surface pressures over 1.0 M KI+0.01 N HCl substrates are summarized in Table I. It will be noted from Table I that at a given temperature k is independent of surface pressure and hence surface concentration. This is also approximately true for the linear portion of the 18°C. plots.

TABLE I

SUMMARY OF RATE CONSTANTS
Substrate: 1.0 M KI+0.01 N HCl

Temperature, °C.	Surface pressure, dynes/cm.	Approximate surface concentration, molecules/cm.^{2} $\times 10^{16}$	Probable film type†	$k \times 10^4$, min.$^{-1}$
10	4.2	3.3	Lc	5.80
	7.8	3.4	Lc	5.80
14	4.2	3.13	Lc	6.85
	12.9	3.47	Lc	7.00
18	3.9	2.68		9.30
	4.3	2.69		9.20
	14.8	3.38		7.70
22.5	7.0	2.78	Le	20.9
25	2.1	2.39	Le	25.3
	15.5	3.09		24.7
35	14.6	—	Le	43.3
	16.8	—	Le	44.9
37	9.9	—	Le	51.1

**Estimated from π–A plots (Fig. 2) on KI-free substrates.*
†Lc = *liquid condensed*; Le = *liquid expanded.*

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The Arrhenius plot for the temperature coefficient of k is given in Fig. 5 and shows two linear portions separated by a discontinuity between 14°C. and 22.5°C. The calculated activation energies are 10.8 kcal./mole in the higher and 8 kcal./mole in the lower temperature range.

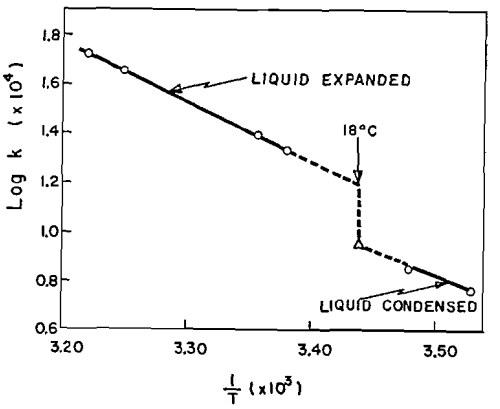

FIG. 5. Arrhenius plot of k for 1.0 M KI+0.01 N HCl substrates.

The variation of k with concentration of KI in the substrate was measured at a surface pressure of 7.7 dynes/cm. and at a temperature of 22.5°C. The experimental values are given in Table II. The rate constant k increases rapidly

TABLE II

INFLUENCE ON k OF KI CONCENTRATION IN 0.01 N HCl SUBSTRATES

Temperature = 22.5°C., surface pressure = 7 dynes/cm.

Concentration KI, moles/liter	$k \times 10^4$, min.$^{-1}$
0.25	4.60
0.5	5.90
1.0	20.9
1.5	24.9

with increase in KI concentration, particularly between 0.5 and 1.0 M, but the order of the reaction in concentration of KI could not be determined.

DISCUSSION

In computing the exchange velocity it is not strictly correct to assume, as above, that the counter detects the radioactive atoms in the surface film but not in the substrate. Time is required for the I^- ions released from the surface to diffuse to a distance beyond which, because of β-particle absorption by the water, they make a negligible contribution to the counting rate. However, if the rate of exchange is much less than the rate of diffusion of I^- ions into the substrate, the method of calculation is acceptable. That this condition prevails can be demonstrated by the following argument.

If it is assumed that the exchange occurs instantaneously, it is possible to

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calculate the decrease with time of the radioactive counting rate that results from diffusion of the radioactive ions away from the surface. The basic equation for diffusion in the substrate may be written

$$\partial C/\partial t = D\partial^2 C/\partial x^2, \quad [4]$$

where C is the volume concentration of radioactive ions at time t at a distance x below the surface, and D is the self-diffusion coefficient of the ions.

If at time $t = 0$, $C = 0$ for all values of x', the solution of Eq. [4] corresponds to that of a one-dimensional diffusion in a semi-infinite system having an instantaneous plane source at $x = 0$ and is given by (23)

$$C = (s/\sqrt{\pi Dt}) \cdot e^{-x^2/4Dt}, \quad [5]$$

where s is the amount of radioactive iodine instantaneously released per unit area of surface.

For simplicity an exponential absorption may be assumed for the β-radiation passing through the substrate to the counter. Then the contribution to the counting rate due to a layer of thickness dx at x is

$$dc(t) = \alpha C \cdot e^{-\mu x} dx, \quad [6]$$

where μ is the absorption coefficient of the substrate and α is a proportionality constant related to counter efficiency and the disintegration constant of the radioactive species.

Combining Eqs. [5] and [6] and integrating yields the total counting rate of the diffusing ions as

$$c(t) = \frac{s}{\sqrt{\pi Dt}} \int_0^\infty \exp\left[-\left(\frac{x^2}{4Dt} + \mu x\right)\right] dx, \quad [7]$$

for which the solution is readily shown to be the remarkably simple relation

$$c(t) = c(0) \cdot e^{-D\mu^2 t}. \quad [8]$$

Eq. [8] is identical with Eq. [3] when $k = D\mu^2$. Taking $D = 1.7 \times 10^{-5}$ cm.^{2}/sec., which is the mean experimental value for I^- in NaI (31), and $\mu = 26.6$ cm.$^{-1}$, which is assumed identical with that of aluminum for the β-radiation of iodine-131 (32), $k = D\mu^2 = 7200 \times 10^{-4}$ min.$^{-1}$. This is several orders of magnitude greater than the values given in Tables I and II. Furthermore D, and therefore $D\mu^2$, is for all practical purposes constant, whereas the experimental values of k increase rapidly with increase in I^- concentration.

It may therefore be safely concluded that exchange rather than diffusion is the rate-controlling step in the process measured.

The values of k $(= V/n)$ in Table I appear to be independent of surface pressure, and hence surface concentration, over the range studied at the indicated temperatures. The exchange reaction is therefore first order in concentration of monolayer molecules.

As noted previously the Arrhenius plot was discontinuous between 14°C. and 22.5°C. (Fig. 5) and the exchange reaction at 18°C. failed to show first

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order behavior over the initial one and one-half to two hours of exchange (Fig. 4). The "critical temperature" for the disappearance of the intermediate-liquid film occurred near this temperature (Fig. 2). The failure of the 18°C. experiments to show the same first order behavior as shown at other temperatures might arise from the simultaneous presence of condensed and expanded liquid films under non-equilibrium conditions on the surface. The over-all exchange velocity would then result from two simultaneous reactions with different rates and associated with the two types of film present.

The discontinuous increase in reaction velocity and activation energy near 18°C. is probably a direct result of the change in surface phase from liquid-condensed to liquid-expanded which occurs in the region of 18°C. Similar discontinuities have been observed by Rideal and others (5, 12, 16, 26) in hydrolysis and oxidation studies in monolayers. The differences in the activation energies were considered by Rideal to arise from changes in the configuration and orientation of monolayer molecules in the surface and hence were attributed to a change in the steric factor of the collision theory treatment of reaction kinetics. The same might apply to the present systems.

Activation energies for homogeneous isotopic halogen exchange in bulk of halogenated acids similar to α-iodostearic acid have been determined. Values of 16 kcal./mole for free α-iodoacetic acid and 17 kcal./mole for the methyl ester have been reported for isotopic iodine exchange with I^- in aqueous solution (29). The value of the activation energy of isotopic bromine exchange between Br^- and α-bromopropionic acid in H_2SO_4 was found to be 20.9 kcal./mole (25). The value of 10.8 kcal./mole found in the present exchange for the expanded film is thus between 5 and 6 kcal./mole lower than the activation energy for similar iodine exchanges in solution. This decrease in activation energy may be associated with a small steric factor for the monolayer exchange in terms of collision theory treatment. In other kinetic studies of monolayer reactions the steric or accessibility factor was found to be essentially unity for reactions involving the α position (22).

Aliphatic halogen exchange reactions are considered to proceed through the mechanism of the Walden inversion (11, 30). The entering halogen ion has been shown to have the greatest probability of substitution if it approaches the carbon atom holding the exchangeable atom from a direction normal to the face of the carbon tetrahedron opposite the atom to be replaced. In monolayers the poor accessibility of this tetrahedron face to the I^- ions might be the cause of the apparent low steric factor in the exchange kinetics, and the change of activation energy observed might be the result of a change in accessibility in going from the condensed to the expanded liquid film.

To obtain the specific rate constant k_s for the exchange reaction the true order of the reaction in monolayer concentration and substrate I^- concentration must be known. Since the reaction is first order in monolayer concentration, the relationship between the over-all velocity and the specific rate constant is given by

$$V = k_s n\, m^y,$$

where m is the concentration of I^- in the substrate and y the order of the reaction with respect to I^-.

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To obtain k_s, the value of y must be determined. In the present investigation it was not possible to determine the true order of dependence on KI concentration. The values of k in Table II do not fit any simple order when the concentration of the substrate solution is used as the effective surface phase concentration. The apparently anomalous dependence of reaction velocity on KI concentration might be resolved if it were possible to calculate the change in concentration in the solution as the monolayer is approached. At present no method exists for calculating the concentration of I^- at the surface; this concentration will depend, among other factors, upon the structure of the electrical double layer existing at the interface.

The behavior of the film itself as the substrate KI concentration is increased must not be overlooked as a possible cause of the anomalous concentration dependence of the exchange. No pressure–area curves could be obtained on KI substrates, and it was assumed that the film characteristics were not greatly changed with increasing KI concentration. This requires experimental confirmation.

While the experimental findings of this investigation are of a preliminary nature and must be extended before further conclusions regarding the detailed mechanism of exchange can be drawn, it is nevertheless considered that these results demonstrate the value of the radioactive tracer method in monolayer systems.

ACKNOWLEDGMENTS

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THE SURFACE ENERGIES OF CALCIUM OXIDE AND CALCIUM HYDROXIDE[1]

By Stephen Brunauer, D. L. Kantro, and C. H. Weise

ABSTRACT

The total surface energies (or surface enthalpies) of calcium oxide and calcium hydroxide were determined by measuring the heats of solution in 2 *N* nitric acid of calcium oxide and calcium hydroxide having high and low specific surface areas, and by determining the surface areas by the B.E.T. method, using nitrogen as adsorbate. The molecular area of nitrogen was taken to be 16.2 Å^2 at 77.3°K. Precision determinations of the lattice parameters indicated that the high and low surface substances had the same unit cell dimensions, and X-ray line broadening measurements indicated that the crystals were perfect or nearly perfect. The surface energy of calcium oxide at 23°C. was found to be 1310±200 erg/cm.^{2}, which compares well with the theoretical value of 1100 erg/cm.^{2} The surface energy of calcium hydroxide at 23°C. was found to be 1180±100 erg/cm.^{2} The heat of the reaction CaO (*c*, 23°)+H_2O (*l*, 23°) = $Ca(OH)_2$ (*c*, 23°), for crystals having negligible specific surface areas, was found to be −15,620 cal.

INTRODUCTION

In 1927 and 1928, Lipsett, Johnson, and Maass (18) published three papers on the surface energy of sodium chloride. They determined the heats of solution of coarsely crystalline and finely divided sodium chloride, measured the surface area microscopically, and obtained the surface energy from the ratio of the energy difference to the difference in surface area. The quantity thus measured is really the surface heat content or enthalpy; however, since Gibbs, it has been customary not to make a distinction between surface enthalpy and total surface energy (or, briefly, surface energy). The investigators concluded, ". . . the surface energy of sodium chloride is found to be about 400 ergs per sq. cm. The errors involved in these measurements are of necessity rather large, and this figure can be regarded as only approximate. It will serve to show, however, the practical applicability of this method to the determination of the surface energy of solids, for which experimental data, so far, are sadly lacking."

The largest error in the above work was in the determination of the surface area of sodium chloride. Only the geometrical surface is visible in the microscope; surface roughnesses of a molecular scale are not visible even in an electron microscope. If the "roughness factor" of the sodium chloride was, let us say, 1.33, the surface area was 33% larger than that measured with the microscope, and the surface energy was only 300 erg/cm.^{2}

Twenty-seven years have passed since 1928, and experimental data on the surface energies of solids are still "sadly lacking". Meanwhile, reliable methods of surface area determination were developed and widely used, yet the problem of the surface energy of sodium chloride is not fully solved to date. The most recent information on the subject is found in a paper of Benson and Benson (1), who prepared sodium chloride samples of widely differing surface areas and determined the surface areas by the B.E.T. method (3), using

[1]*Manuscript received February 2, 1956.*
Contribution from the Portland Cement Association Research and Development Laboratories, Chicago, Illinois.

nitrogen as the adsorbate. Because of slight quantities of impurities, the effects of which on the surface energy the authors were unable to estimate, they regarded their surface energy value of 305 erg/cm.^{2} as "provisional". If the effects of impurities on the heats of solution were additive, the value of Benson and Benson must be close to the true surface energy of sodium chloride.

The only other reliable experimental surface energy value published so far is that of Jura and Garland (14) for magnesium oxide. In this case, also, the authors pointed out that their surface energy value may have been in error; and in the light of the results reported in this paper, their value for magnesium oxide does appear to be somewhat too low.

Theoretical evaluations of the surface energies of certain ionic crystals, crystallizing in cubic lattices, were made by a number of investigators, but these are only rough approximations. The scarcity of data on surface energies is so much the more surprising, since the interest in surface chemistry in general, and in adsorption in particular, has tremendously increased in the last decade and a half. Energy changes occurring in adsorption were widely investigated, but the investigators usually interpreted the changes as being due to a change in state of the adsorbate and assumed, for convenience, that the change in state of the surface of the adsorbent was negligible. The theoretical arguments advanced in favor of this assumption were inadequate, and experimental data were wholly lacking. It seems that a systematic investigation of the energy contents of a variety of surfaces could throw some light on this problem. It could, probably, also furnish some useful information as to the validities of various theories advanced for the structures of solid surfaces, such as, for example, the theory developed by Weyl (30).

In the present investigations, the surface energies of calcium oxide and calcium hydroxide were obtained by determining the heats of solution in 2 *N* nitric acid of samples having different surface areas, and measuring the surface areas by the B.E.T. method (3), using nitrogen as the adsorbate.

EXPERIMENTAL

Calcium Oxide

The low surface calcium oxide, Batch A-40, was prepared from Fisher's certified reagent grade calcium carbonate. The calcium carbonate was ignited at 1050°C. for four hours, cooled, and pressed into pellets, $\frac{1}{4}$ in. in diameter and $\frac{1}{4}$ in. to $\frac{3}{8}$ in. long, by a Parr pellet press. The pellets were then ignited at 1300°C. for 64 hr., and cooled and stored in a desiccator containing phosphorus pentoxide. Prior to use, each sample was ignited at 1050°C. for 30 min., cooled in a phosphorus pentoxide desiccator, weighed, and then introduced immediately into the calorimeter or the adsorption apparatus.

The high surface calcium oxide, Batch A-39, was prepared from calcium hydroxide, Batch E-4. Each sample was separately prepared before use. The calcium hydroxide was ignited at 1050°C. for 30 min., cooled for 15 min. over fresh phosphorus pentoxide in a desiccator, weighed, reignited at 1050°C. for 15 min., again cooled for 15 min., then immediately introduced into the calorimeter or the adsorption apparatus. The samples were not weighed after

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the second ignition. The first ignition always gave the correct ignition loss, and it was assumed that the weight after the second ignition was the same as after the first ignition. A single ignition, with subsequent weighing, gave far less reproducible results.

In handling both calcium oxide and calcium hydroxide, extreme precautions were taken to avoid contamination of the materials by atmospheric moisture and carbon dioxide. To the extent possible, all operations, including pelleting, were carried out in a controlled-atmosphere cabinet.

All samples of calcium oxide and calcium hydroxide were exposed to the atmosphere only while they were being dropped into the calorimeter, which period never exceeded five seconds. To ascertain the amount of moisture picked up in this short time, the following experiment was performed. (1) A 1 gm. sample of calcium oxide, A-39, was prepared as described above. (2) After the final cooling period, the covered platinum crucible with the sample was transferred from the desiccator into a weighing bottle inside the controlled-atmosphere cabinet. (3) The weighing bottle, with its contents, was weighed. (4) The sample was exposed to the atmosphere over the calorimeter bath for five seconds. The crucible was then covered, returned to the weighing bottle, the weighing bottle was covered, and the weight was determined. (5) The procedure of step (4) was repeated three times, except that each exposure interval was 20 sec.

The experiment was performed on three separately prepared samples, with the result that the amount of moisture picked up in five seconds was *at most* 0.13 mgm./gm. Actually, no gain in weight occurred in the first five seconds, probably because time was needed for the moisture to reach the sample after the opening of the crucible. It is possible that a shorter time delay would have occurred if the sample had been dropped into the calorimeter funnel. The moisture gain was very close to linear with time between 5 sec. and 45 sec., with a slope of 0.13 mgm./gm. per 5 sec.

Calcium Hydroxide

The coarsely crystalline calcium hydroxide, Batch E-4, was prepared in a manner similar to that employed at the National Bureau of Standards (20). A 100 ml. beaker, filled with saturated sodium hydroxide solution, and a 150 ml. beaker, filled with saturated calcium nitrate solution, were placed in a large jar. Both chemicals were Baker's analyzed reagent grade, and deionized water was used. Water was then added to the jar until the liquid level was about one inch above the level of the taller beaker. Care was taken to avoid mixing. The jar was covered, and was left standing undisturbed for about two weeks, by which time a growth of calcium hydroxide crystals practically filled the mouth of the beaker containing the calcium nitrate solution. The calcium hydroxide crystals were removed from the beaker in the controlled-atmosphere cabinet, washed several times with water, and dried overnight at a water vapor pressure of 0.5 μ of mercury. The dry calcium hydroxide was sieved in the cabinet; the fraction passing a U.S. Standard No. 30 sieve was discarded, and the rest was stored in paraffin-sealed weighing bottles until used.

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The high surface calcium hydroxide, Batch E-8, was prepared by vapor phase hydration of calcium oxide in a manner similar to that described by Thorvaldson and Brown (26). Fisher's certified reagent grade calcium carbonate was ignited at 1050°C. for four hours, cooled in a desiccator containing phosphorus pentoxide, and crushed in the controlled-atmosphere cabinet to pass a U.S. Standard No. 100 sieve. The calcium oxide was then distributed among several tared polyethylene weighing bottles, which were placed over water in a desiccator jar. The bottles were weighed periodically. When the water content had risen to a value 35% in excess of the stoichiometric quantity, the material was removed and dried at a water vapor pressure of 0.5 μ of mercury. The dry calcium hydroxide was pressed into pellets, $\frac{1}{4}$ in. in diameter and $\frac{1}{4}$ in. to $\frac{3}{8}$ in. long, in a Parr pellet press inside the controlled-atmosphere cabinet, and the pellets were stored in paraffin-sealed weighing bottles until used.

After vacuum drying and pelleting, Batch E-8 contained 0.76% excess water. This corresponded approximately to a quantity of water sufficient to cover the entire surface of the calcium hydroxide with an adsorbed monolayer of water. To obtain a sample with less excess water, half of Batch E-8 was heated at 180° to 200°C. for 16 hr. in a vacuum of the order of 10^{-6} mm. of mercury. The batch, E-8A, contained only 0.12% excess water, but the heating resulted in some sintering. The pellets were stored in paraffin-sealed weighing bottles until used.

An experiment similar to that performed on calcium oxide, and described in the previous section, was made on calcium hydroxide, Batch E-8A, to ascertain the water pickup during the five seconds of introduction of the sample into the calorimeter. The amount of water picked up was less than 0.1 mgm./gm.

X-Ray Measurements

X-Ray powder diffraction patterns were obtained by means of a North American Philips wide range Geiger counter diffractometer. The basic unit was operated at 40 kv. and 20 ma. Copper K_α radiation was used; the K_β component was removed by a nickel filter. For precision determinations of the lattice parameters, the goniometer scanning rate was $\frac{1}{4}$°/min. and the chart speed was 1 in./min., so that readings could be made to the nearest 0.02°2θ.

For each calcium oxide sample six lines and for each calcium hydroxide sample seven lines were recorded in the back-reflection region. Relative intensities (I/I_1) and (hkl) assignments were taken from the data of Swanson and Tatge (25). It was found that the calcium hydroxide reflection corresponding to a d spacing of 0.8140 Å was incorrectly assigned. The (hkl) values should be (312) rather than (006).

For calcium oxide, plots of a_0 vs. $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$ (15) gave good straight lines, regardless of specific surface area and crystallite size. In the case of calcium hydroxide, there were not enough ($hk0$) and no ($00l$) reflections to permit single parameter evaluations. All unambiguous reflections in the range

d = 1.13 to 0.814 were, therefore, used, and a_0 and c_0 were obtained by least squares calculations (16). Statistical weights were assigned proportional to $(I/I_1)\tan^2\theta/d^2$, and the systematic errors were assumed to have the same angular dependence as those found for calcium oxide.

For the line broadening investigations, a scanning rate of $\frac{1}{8}$°/min. was used. The broadening of the calcium oxide line at 2.405 Å (100) and of the calcium hydroxide lines at 3.11 Å (100) and 4.91 Å (001) was measured. The crystallite dimensions were calculated by means of Scherrer's equation (22).

Other Operations

Ignition loss and carbon dioxide content were determined and chemical analyses were performed according to the methods described by Brunauer, Hayes, and Hass (4).

The calorimeter was essentially the same as that of Verbeck and Foster (28), with the modifications described by Brunauer, Kantro, and Weise (5). The acid solvent was 420 gm. of 2 N nitric acid.

Surface areas were measured by the B.E.T. method (3), using nitrogen at 77.3°K. Corrections for deviations from the perfect-gas law were taken from Emmett and Brunauer (8).

RESULTS

The experimental calorimetric results for calcium oxide and calcium hydroxide are shown in Table I. These results were then corrected for impurities.

TABLE I

HEATS OF SOLUTION OF CALCIUM OXIDE AND CALCIUM HYDROXIDE

CaO(A-40)		CaO (A-39)		$Ca(OH)_2$ (E-4)		$Ca(OH)_2$ (E-8)		$Ca(OH)_2$ (E-8A)	
Weight (gm.)	ΔH (cal./gm.)	Weight (gm.)	ΔH (cal./gm.)	Weight (gm.)	ΔH (cal./gm.)	Weight (gm.)	ΔH (cal./gm.)	Weight (gm.)	ΔH (cal./gm.)
1.0011	844.32	1.0043	847.54	0.6510	428.35	1.1506	428.02	1.0046	432.94
1.0065	845.42	1.0062	846.45	0.8255	427.26	1.2862	428.44	1.0100	432.77
1.0408	845.36	1.1379	848.16	0.8568	427.92	1.3668	427.63	1.0330	432.73
1.3427	844.99	1.3607	847.20	0.8866	428.68	1.3863	428.02	1.1325	432.17
1.3497	844.42	1.3624	846.51	1.0110	428.25	1.4760	427.97	1.3358	433.01
1.3503	844.26	1.3692	846.04	1.0198	427.67	1.5511	428.72	1.3606	432.32
1.3512	844.40	1.3828	847.66	1.0708	428.29				
1.3598	844.61			1.2286	427.39				
				1.2871	427.16				
				1.3673	428.71				
				1.4374	427.90				
				1.6253	428.13				
				1.7913	428.41				
Average = 844.72		847.08		428.01		428.13		432.66	
Std. error = 0.17		0.29		0.14		0.18		0.16	

Only impurities amounting to 0.01% or more were considered. Both batches of calcium oxide contained 0.01% sodium oxide; in addition, calcium oxide, Batch A-40, contained 0.05% magnesium oxide. The following impurities were found in the three batches of calcium hydroxide: in E-4, 0.01% sodium hydroxide and 0.13% calcium carbonate; in E-8, 0.01% sodium hydroxide, 0.07% magnesium hydroxide, 0.36% calcium carbonate, and 0.76% water; in E-8A, 0.01% sodium hydroxide, 0.07% magnesium hydroxide, 0.27% calcium carbonate, and 0.12% water. The following values were used for the

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heats of solution of the impurities, in cal./gm.: sodium oxide, 1346; sodium hydroxide, 590; magnesium oxide, 865; magnesium hydroxide, 446; and calcium carbonate, 86. The corrections for water in calcium hydroxide, Batches E-8 and E-8A, will be discussed later.

Corrected values of the heats of solution, in cal./gm., exclusive of the heat evolved in the uptake of excess water, were as follows: calcium oxide, Batch A-40, 844.67; calcium oxide, Batch A-39, 847.03; calcium hydroxide, Batch E-4, 428.44; calcium hydroxide, Batch E-8, 432.64; and calcium hydroxide, Batch E-8A, 434.05.

Surface areas of the five substances, in meters^2/gm., were as follows: calcium oxide, Batch A-40, 0.3; calcium oxide, Batch A-39, 7.8; calcium hydroxide, Batch E-4, 0.1; calcium hydroxide, Batch E-8, 26.1; and calcium hydroxide, Batch E-8A, 21.8. It was assumed that one nitrogen molecule covered an area of 16.2 Å^2.

The two batches of calcium oxide gave identical values for the lattice parameter a, the edge of the unit cube, the value being 4.8108 ± 0.0002 Å. For the three batches of calcium hydroxide, the parameters of the hexagonal lattice were: Batch E-4, $a = 3.5933\pm0.0003$ Å, $c = 4.9086\pm0.0021$ Å; Batch E-8, $a = 3.5929\pm0.0006$ Å, $c = 4.9078\pm0.0046$ Å; and Batch E-8A, $a = 3.5926\pm0.0003$ Å, $c = 4.9082\pm0.0026$ Å. The determinations were made at 26°C.

The X-ray line broadening measurements gave the following results: On the basis of the half-intensity width of the 2.405 Å line of calcium oxide, Batch A-40, as standard, the broadening of that line of Batch A-39 was $0.030°2\theta$. With the half-intensity widths of the 3.11 and 4.91 Å lines of calcium hydroxide, Batch E-4, as standards, the broadening of the 3.11 Å lines of Batches E-8 and E-8A were 0.085 and $0.070°2\theta$, respectively; and the broadening of the 4.91 Å lines of E-8 and E-8A were 0.105 and $0.1325°2\theta$, respectively.

DISCUSSION

The Surface Energy of Calcium Oxide

1. In order to be reasonably certain that the energy difference between the two batches of calcium oxide was due to the difference between the specific surface areas *alone*, it had to be ascertained whether the bodies of the crystals had identical structures. This was accomplished (1) by precision determinations of the lattice parameter and (2) by X-ray line broadening measurements. The former showed that the lattice parameters a of the high and low surface calcium oxide were identical to the fifth significant figure. The identity is subject to an uncertainty of only 2×10^{-12} cm. in each determination, or one part in 24,000. Thus, the spacings of the ions in both batches of calcium oxide were found to be identical. The X-ray line broadening measurements, to be discussed in detail later, indicated that the crystals of both batches were either almost perfect, or, if not, the imperfections were of the same kind and extent.

2. The two batches of calcium oxide were prepared by widely differing methods: A-40 was "hard burned" lime, obtained by igniting calcium carbonate at 1300°C. for 64 hr., whereas A-39 was soft burned lime, obtained by igniting

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calcium hydroxide at 1050°C. for 45 min. It is a well-known fact that hard burned lime reacts with water very slowly. The two batches of calcium oxide showed a marked disparity in their rates of reaction with 2 *N* nitric acid. It is clear from the X-ray results that this could not have been caused by differences in crystal densities (and, by implication, by differences in bond strengths), nor by crystalline imperfections. Very probably, the disparity in rate was caused by the difference between the specific surface areas of A-39 and A-40.

3. The corrected heat of solution of A-39 was 847.03 cal./gm., with a standard error of 0.17 cal./gm.; that of A-40 was 844.67 cal./gm., with a standard error of 0.29 cal./gm. The difference between the heats of solution was 2.36 cal./gm., with a standard error of 0.34 cal./gm. The surface area of A-39 was 7.8 meters^2/gm.; that of A-40 was 0.3 meters^2/gm. The difference was 7.5 meters^2/gm., and the uncertainty in the difference was 0.1 meters^2/gm. *The calculated surface energy of calcium oxide at 296°K. was 1310±200 erg/cm.*^{2}

In addition to the errors mentioned above, there are two other possible sources of error to be considered. The molecular area of nitrogen at 77.3°K. was assumed to be 16.2 Å^2. Livingston (19) proposed an area of 15.4 Å^2. If Livingston's figure is correct, the surface energy of calcium oxide is 70 erg/cm.^{2} *higher* than the value given above. The area of 16.2 Å^2 was used by Brunauer, Emmett, and Teller (3), and it was confirmed by Harkins and Jura (12) by means of a totally different approach.

A second source of error may have come from an uptake of water by calcium oxide, Batch A-39, during the introduction of the sample into the calorimeter. In the experimental part, the method used to estimate the magnitude of this effect was described. It is possible that no water was picked up during the less than five seconds of addition; if there was any uptake, it was at most about 0.13 mgm./gm. (A monolayer of water would correspond to 2.20 mgm./gm., using a molecular area of 10.6 Å^2.) Jura and Garland (14) found that when magnesium oxide sorbed an amount of water sufficient to form half a monolayer, the heat evolved per mole of water was about equal to the heat of hydration of magnesium oxide. If it is assumed that the same is true for calcium oxide, the heat evolved in the sorption of 0.13 mgm. of water would be 0.11 cal. A correction for this effect would *raise* the surface energy of calcium oxide by 60 erg/cm.^{2}

The above errors may or may not exist, but even if they do, they are relatively small. If both were present, the surface energy would be raised by a *maximum* of 130 erg/cm.^{2} Not knowing whether or not these errors were present, no attempt was made to correct for them. It is clear, however, that a more cautious estimate of the surface energy of calcium oxide would be 1375± 250 erg/cm.^{2}

4. Lennard-Jones and Taylor (17) calculated the surface energy of the (100) face of calcium oxide at 0°K. and obtained 1032 erg/cm.^{2} Jura and Garland found experimentally that the surface energy of magnesium oxide increased by 50 erg/cm.^{2} in the temperature range from 0° to 298°K. Because of the similarity between calcium oxide and magnesium oxide, it may safely be

assumed that the surface energy of calcium oxide at room temperature is also larger than the 0°K. value by the same amount. Thus, the theoretical surface energy of calcium oxide at 23° would be about 1100 erg/cm.^{2} The experimental value is 1310±200 erg/cm.^{2} The agreement between theory and experiment is, therefore, quite good.

The agreement between the experimental and theoretical surface energy of magnesium oxide is reasonably good. Jura and Garland obtained 1100 erg/cm.^{2} for the former, and Lennard-Jones and Taylor obtained 1362 erg/cm.^{2} for the latter. The value of Jura and Garland is probably too low. Since the surface energy of even calcium hydroxide appears to be greater than 1100 erg/cm.^{2}, it seems improbable that that of calcium oxide should be less than this value. On the basis of theory, the surface energy of magnesium oxide should be about 300 erg/cm.^{2} larger than that of calcium oxide, or at least 1400 erg/cm.^{2} Jura and Garland pointed out that they were unable to estimate the amount of water picked up by the magnesium oxide samples in the course of introducing them into the calorimeter. It is possible that their high surface magnesium oxide picked up enough water and carbon dioxide from the atmosphere to account for the somewhat low result.

The agreement between the theoretical and experimental surface energies of calcium oxide and magnesium oxide is so much the more surprising, since the experimental surface energy obtained for sodium chloride is twice as large as the best theoretical value, calculated by Shuttleworth (23).* Recently, van der Hoff and Benson (13) calculated the surface energy of lithium fluoride on the basis of a quantum mechanical model, instead of the "classical" model used by earlier investigators. They obtained a surface energy value almost three times as large as that based on the classical model. It seems that it would be desirable to recalculate the surface energies of calcium oxide and magnesium oxide on the basis of quantum mechanical models.

The Surface Energy of Calcium Hydroxide

1. The lattice parameters of the three batches of calcium hydroxide were given under "Results". The precision attained in the evaluation of the two parameters was somewhat smaller than that obtained for the single lattice parameter of calcium oxide. Since the differences are not statistically significant, it can be concluded that all three batches of calcium hydroxide had the same a and the same c parameters, indicating the same spacings of the ions in the crystals. The X-ray line broadening measurements, to be discussed in detail later, indicated that the crystals of all three batches were either almost perfect or, if not, the imperfections were of the same kind and extent.

In spite of the above facts, the differences between the heats of solution of E-4 and E-8 on the one hand, and between E-4 and E-8A on the other, were not caused by differences in surface energy *alone*. Both E-8 and E-8A contained some excess water, and the differences between the heats of solution were

*G. C. Benson and R. McIntosh (*Can. J. Chem. 33: 1677. 1955*) recently pointed out that the agreement between the theoretical value of Lennard-Jones and Taylor and the experimental value of Jura and Garland for the surface energy of magnesium oxide is probably fortuitous. In the theoretical calculations, the van der Waals term was neglected and the repulsive term was calculated in a questionable manner. The same criticism applies to the theoretical calculation of the surface energy of calcium oxide.*

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partly caused by the heat of sorption of water. It is possible that the water was occluded in the lattice, and it is possible that it was adsorbed on the surface. Corrections for the water were attempted both ways and, as will be seen, both types of correction led to the same result.

2. Calcium hydroxide, Batch E-4, contained no excess water, Batch E-8A contained 0.12%, and Batch E-8 contained 0.76% excess water. The fact that the lattice parameters of the three batches were the same made it unlikely that the water was dissolved in the lattice. Nevertheless, it is possible that some water can be dissolved in the calcium hydroxide lattice without changing its dimensions, and it is also possible that the dimensions of the three batches were actually slightly different, even though in the present experiments the differences could not be detected. At any rate, calculations were made on the basis of the assumption that the water was dissolved in the lattices of E-8 and E-8A.

The corrected heat of solution of E-4 was 428.44 cal./gm.; the heats of solution of E-8 and E-8A, corrected for all impurities but uncorrected for the heat of sorption of excess water, were 432.64 and 434.05 cal./gm., respectively. The surface areas of E-4, E-8, and E-8A were 0.1, 26.1, and 21.8 meters^2/gm., respectively. By assuming that the heat evolved in the solution of water in the calcium hydroxide lattice is proportional to the amount of water dissolved, one can calculate from the above data both the heat of solution of water and the surface energy. The heat evolved in the solution was found to be 412 cal./gm. of water (or 7420 cal./mole of water), and the surface energy of calcium hydroxide was 1180 erg/cm.^{2}

3. It seems more likely that the excess water in Batches E-8 and E-8A was adsorbed water. Since there are no data available on the heats of adsorption of water on calcium hydroxide, the values were estimated on the basis of the fact that the heats of physical adsorption of water on a variety of surfaces show striking similarities.

The amount of excess water in Batch E-8 corresponded to a monolayer of adsorbed water, provided the area of a water molecule is assumed to be 10.3 Å^2. Although this value is somewhat smaller than the 10.6 Å^2 obtained from the density of liquid water, such a close packing on the surface does not seem unreasonable. Harkins and Jura (11) found that the integral net heat of adsorption of water on anatase (titanium dioxide), at an amount of water adsorbed equal to a monolayer, was 6550 cal./mole of water. Copeland (6) found in this laboratory that the integral net heat of adsorption of water on *hydrated* portland cement under the same condition was 6640 cal./mole. If one takes the average, 6600 cal./mole, as a reasonable value for the integral net heat of adsorption of water on calcium hydroxide at an adsorption equal to a monolayer, the water correction of the heat of solution of Batch E-8 is 2.78 cal./gm. This value is to be added to the difference between the heats of solution of E-8 and E-4, 4.20 cal./gm. The difference between the surface areas of E-4 and E-8 was 26.0 meters^2/gm. The calculated surface energy of calcium hydroxide was 1120 erg/cm.^{2}

As stated earlier, the heating of E-8 resulted in some sintering, the surface area decreasing from 26.1 to 21.8 meters^2/gm. If one assumes a molecular

area of 10.3 Å^2 for water, 6.33 mgm. of water would cover 1 gm. of E-8A with an adsorbed monolayer. The water content of E-8A was 1.2 mgm. per gm., corresponding to a surface coverage of 19%. The heat of adsorption of this water was estimated in the following manner. The integral net heat of adsorption of water on various surfaces was plotted against θ, the fraction of the surface covered. The data of Harkins and Jura (11) for anatase, those of Powers and Brownyard (21) and Copeland (6) for hydrated portland cement, and some data by the authors of this paper for hydrated tricalcium silicate fell on a single curve. The integral net heat of adsorption at $\theta = 0.19$ was 12,500 cal./mole. Assuming that this is a reasonable value for a calcium hydroxide surface as well, the water correction of the heat of solution of Batch E-8A is 0.83 cal./gm. This value is to be added to the difference between the heats of solution of E-8A and E-4, 5.61 cal./gm. The difference between the surface areas of E-8A and E-4 was 21.7 meters^2/gm. The calculated surface energy of calcium hydroxide was 1240 erg/cm.^{2}

The surface energy obtained from the data on E-4 and E-8 was found to be 1120 erg/cm.^{2}, and that obtained from the data on E-4 and E-8A was 1240 erg/cm.^{2} The average of the two is 1180 erg/cm.^{2} The value obtained on the basis of the assumption that the excess water was dissolved in the lattice of calcium hydroxide was also 1180 erg/cm.^{2}

4. Whether the excess water was dissolved or adsorbed, the conclusion is that *the surface energy of calcium hydroxide at 296°K. is 1180 erg/cm.^{2} The uncertainty, estimated below, is ±100 erg/cm.^{2}*

The standard errors of the average heats of solution for the three batches of calcium hydroxide were given in Table I. The standard error in the surface area of Batches E-8 and E-8A is ±0.2 meters^2/gm. These errors lead to an uncertainty of ±50 erg/cm.^{2} in the surface energy. Uncertainties in the corrections for impurities other than water introduce an additional error of ±15 erg/cm.^{2} The error in the water correction may be as high as 40 erg/cm.^{2} For the heat of adsorption of water on E-8A the value of 12,500 cal./mole was assumed. The heat of adsorption of water on calcium hydroxide is probably not as high as the heat of reaction of calcium oxide with water; nevertheless, if the value of 15,600 cal./mole is used for the heat of adsorption, the surface energy of calcium hydroxide calculated from the data of E-8A would be raised by 40 erg/cm.^{2}

The above errors together amount to an uncertainty of about 100 erg/cm.^{2} This does not take into account the uncertainty in the molecular area of nitrogen, discussed before. If Livingston's (19) value is correct, the surface energy of calcium hydroxide would be raised by 5%, or about 60 erg/cm.^{2} Nor does the 100 erg/cm.^{2} error include the possible error caused by an uptake of water during the introduction of the calcium hydroxide into the calorimeter. This error may amount to as much as 15 erg/cm.^{2} A cautious estimate of the surface energy of calcium hydroxide would be 1220±150 erg/cm.^{2}

5. The only surface energy value in the literature with which the present value for calcium hydroxide can be compared is that obtained by Fricke, Schnabel, and Beck (9) for magnesium hydroxide. Their value of 330 erg/cm.^{2}

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seems to be too low by a factor of 3, at least. They estimated the specific surface areas of their magnesium hydroxide samples by means of X-ray line broadening measurements, and the greatest part of the line broadening may have been caused by crystalline imperfections, rather than by dimensions. This point will be further discussed later.

One would intuitively expect that the surface energy of calcium hydroxide should be somewhere between the surface energies of calcium oxide, 1310 erg/cm.^{2}, and water, 118.5 erg/cm.^{2} (11). (There is no surface energy value available for ice.) The value of 1180 erg/cm.^{2} is actually between those limits, and it is quite close to the surface energy of calcium oxide. Perhaps this result is not too surprising. The non-specificity that one finds in physical adsorption is primarily due to the fact that the predominating factor is the change in the state of the adsorbate. Nevertheless, when one encounters such a *high degree* of non-specificity as found, for example, in the already discussed heats of adsorption of water on *anhydrous* and *hydrated* surfaces, the cause is probably to be found not merely in the identity of the adsorbate but also in the similarities between the surface energies of the adsorbents. Likewise, such dissimilarities as were found, for example, by Harkins and Boyd (10) in the heats of wetting of various ionic surfaces by water were probably caused by dissimilarities in the energies (both free and total) of those surfaces.

6. Jura and Garland (14) found that the free surface energy of magnesium oxide was 90 erg/cm.^{2} less than its total surface energy at room temperature. Because of the similarity of calcium oxide to magnesium oxide, it is probable that the free surface energy of calcium oxide is also about 100 erg/cm.^{2} less than its surface energy, or about 1200 erg/cm.^{2} In general, the entropies of solid surfaces seem to be low; thus, at room temperature the free surface energy differs only slightly from the total surface energy. A value of 1100 erg/cm.^{2} for the free surface energy of calcium hydroxide is probably close to the true value.

X-Ray Line Broadening and Surface Area

1. The broadening of X-ray diffraction lines is caused either by crystalline imperfections, such as, for example, mosaic structure (7), or by small dimensions of the crystals. Scherrer (22) was the first to show how mean dimensions of the crystallites can be calculated from line broadening. Naturally, this can be done only if the broadening caused by imperfections is negligible compared to the broadening caused by crystal size. This appeared to be true or nearly true for the calcium oxide and calcium hydroxide crystals used in the present investigations, since the surface areas calculated from line broadening measurements were, within the errors involved, about the same as those obtained from nitrogen adsorption.

2. The 2.405 Å line of calcium oxide is the (100) reflection; the dimension calculated from the broadening of this line is, therefore, that of the edge of the average cube. It follows from Scherrer's formula that

$$\frac{B}{93.11} = \frac{1}{D_{A\text{-}39}} - \frac{1}{D_{A\text{-}40}}$$

where B is the difference between the half intensity widths of the 2.405 Å lines of A-39 and A-40 in degrees of 2θ, and $D_{A\text{-}39}$ and $D_{A\text{-}40}$ are the lengths of the edges of the average cubes of A-39 and A-40 in Ångstrom units, respectively.

Using 3.345 gm./cc. for the density of calcium oxide and 0.3 meters^2/gm. for the specific surface area of A-40, one obtains the value of 5.98 μ for $D_{A\text{-}40}$. Since $B = 0.030°$ (see "Results"), $D_{A\text{-}39} = 2950$ Å. If it is assumed that A-39 was composed of cubes of equal sizes, calculation leads to the results that (*a*) 1 gm. of A-39 contained 1.16×10^{13} cubes, and (*b*) the specific surface area was 6.1 meters^2/gm. The surface area obtained by nitrogen adsorption was 7.8 meters^2/gm. Thus, line broadening indicated a surface area 22% *smaller* than nitrogen adsorption did.

3. Similar calculations were made for the two high-surface calcium hydroxide batches, E-8 and E-8A. In this case, it was assumed that the calcium hydroxide crystallites were hexagonal prisms, and the height of the average prism was obtained from the broadening of the 4.91 Å line (001), and the side of the hexagon was calculated from the broadening of the 3.11 Å line (100). The density of calcium hydroxide was taken to be 2.241 gm./cc., and the specific surface area of E-4 (used as standard), 0.1 meters^2/gm. The height of the average prism was found to be 845 Å for E-8 and 670 Å for E-8A, and the side of the average hexagon 1230 Å for E-8 and 1495 Å for E-8A. If it is assumed that E-8 was composed of hexagonal plates of equal sizes, and a similar assumption is made for E-8A, calculations lead to the results that (*a*) 1 gm. of E-8 contained 1.34×10^{14} and 1 gm. of E-8A, 1.15×10^{14} plates, and (*b*) the specific surface area of E-8 was 18.9 and that of E-8A, 20.2 meters^2/gm. The specific surface areas thus obtained for E-8 and E-8A are *smaller* than the nitrogen adsorption areas by 28 and 7%, respectively.

4. It is to be noted that in all three instances line broadening gave smaller surface areas than nitrogen adsorption did. The reason for this is found in the fact, experimentally demonstrated by Birks and Friedman (2), that line broadening gives greater weights to the large particles than to the small ones. It seems clear from their results, as well as from the present data, that the surface area calculated from the average dimensions, obtained from X-ray line broadening, will, in general, be smaller than the true surface area for polydisperse systems, *provided that the line broadening is caused by the dimensions of the crystals alone*. Line broadening can give an accurate value for the surface area only for monodisperse systems, just as nitrogen adsorption can give the correct particle size only for monodisperse systems.

In the majority of cases published in the literature, the surface areas calculated from line broadening were *larger* than those determined by nitrogen adsorption. It is very likely that in these instances the broadening was not caused by crystal size alone but by a combination of size and crystalline imperfections.

5. It follows from the above considerations that care must be exercised in calculating surface areas from line broadening. For example, the large apparent surface area value obtained by Fricke, Schnabel, and Beck (9) for magnesium hydroxide, discussed earlier, was probably caused by imperfections in the

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crystals. Another example is found in some of the results obtained for calcium hydroxide, Batches E-8 and E-8A. The latter was obtained by heating the former at 180° to 200° for 16 hr. The nitrogen adsorption clearly indicated sintering, the surface area having decreased from 26.1 to 21.8 meters²/gm. However, the surface area calculated from line broadening showed a reverse effect; it increased on heating from 18.9 to 20.2 meters²/gm. This is, obviously, a false result.

6. Nevertheless, some interesting speculations can be made on the basis of the line broadening measurements. Heating resulted in a decrease in the number of crystallites per gram of calcium hydroxide by about 14%. This is an indication of sintering. The crystallites that disappeared must have been the smallest ones. The resulting material must have been more nearly monodisperse than the initial material, from which it follows that there should be a better agreement between the X-ray surface and the nitrogen surface for E-8A than for E-8. This was actually true; the X-ray surface of E-8 was 28% smaller than the nitrogen surface, whereas the X-ray surface of E-8A was only 7% smaller. The agreement between the X-ray surface and the nitrogen surface obtained for E-8A is quite striking. It would become even more striking if one would use Livingston's (19) value for the adsorption area of a nitrogen molecule. In that case the two would differ only by 2%.

The slight sintering resulted in some flow of the material. Line broadening showed that the flat plates had become thinner; the average height of the hexagonal plates of E-8 was 845 Å, that of E-8A was 670 Å.

7. All dimensions in this section were calculated by means of Scherrer's formula (22). Warren (29) also proposed a formula for the calculation of crystal dimensions from line broadening. For calcium oxide, Batch A-39, Scherrer's formula led to a value of 2950 Å for the edge of the average cube, whereas Warren's formula led to 860 Å. The former value gave a surface area 22% smaller than the nitrogen adsorption area, the latter gave an area 2.8 times larger. It seems, therefore, that for the types of systems investigated, Warren's formula is not applicable. No attempt was made to use the method of Stokes (24).

The Heat of Hydration of Calcium Oxide

A by-product of the present investigations was a value for the heat of the reaction

$$CaO\ (c, 23°) + H_2O(l, 23°) = Ca\ (OH)_2\ (c, 23°)$$

for the case when both the calcium oxide and calcium hydroxide crystals have negligible surface areas. The heat of solution of calcium oxide, Batch A-40, was 844.67 cal./gm. The surface area of this batch was 0.3 meters²/gm. Correcting to zero surface gave a heat of solution of 844.58 cal./gm. The heat of solution of calcium hydroxide, Batch E-4, was 428.44 cal./gm., and the surface area was 0.1 meters²/gm. Correcting to zero surface gave a heat of solution of 428.42 cal./gm. From these values, it follows that

$$\Delta H_{296} = -15{,}620 \text{ cal.}$$

The estimated uncertainty is ±20 cal. Thorvaldson, Brown, and Peaker (27) obtained the value of −15,640 cal. for ΔH_{293} by determining the heats of solution of calcium oxide and calcium hydroxide in hydrochloric acid, and −15,490 cal., by measuring directly the heat evolved in the hydration of calcium oxide. They gave preference to the former value, and the present result confirms the correctness of their choice.

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AMINO ACIDS

III. CYCLIC GUANIDINO ACIDS AND THEIR DERIVATIVES[1]

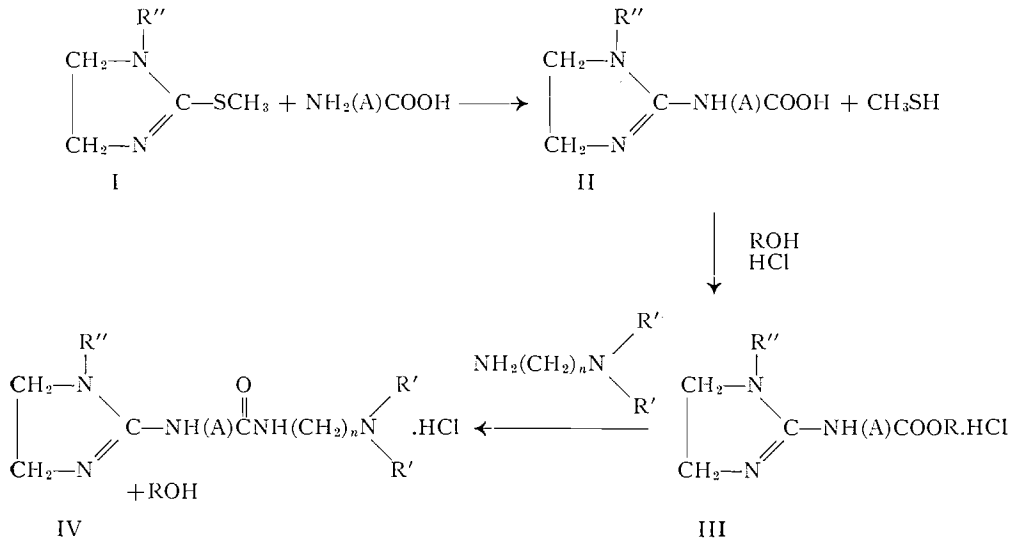
By D. L. Garmaise,[2] S. O. Winthrop,[3] Gordon A. Grant,[3] and A. F. McKay[2]

ABSTRACT

Several new cyclic guanidino acids have been prepared by the reaction of cyclic isothioureas with amino acids. The ethyl esters of some of these acids have been converted into dialkylaminoalkylamides by refluxing with dialkylaminoalkylamines in the presence of an inert solvent. A series of dialkylaminoethyl esters of the 2-(carboxyalkylamino)-2-imidazolines also have been prepared.

The reaction (3) of amino acids with cyclic isothioureas (I) provides a convenient method for the preparation of 2-(carboxyalkylamino)-2-imidazolines (II) (or the tautomeric 2-(carboxyalkylimino)-imidazolidines). These imidazoline derivatives are prepared most conveniently in the laboratory by refluxing the free base of a 2-methylmercapto-2-imidazoline and an amino acid in the presence on an inert solvent such as methanol or benzene. In this manner, the products have been obtained in yields as high as 96%.

Some difficulty has been experienced with the esterification of the 2-(carboxyalkylamino)-2-imidazolines (II). The yields of ester hydrochlorides (III) vary considerably although yields as high as 83% have been obtained. A



A = alkylene group R = alkyl or dialkylaminoethyl R′ = alkyl R″ = H or $-CH_2CH_2OH$

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Contribution from the L. G. Ryan Research Laboratories of Monsanto Canada Limited, Ville LaSalle, Quebec, and Research and Biological Laboratories of Ayerst, McKenna and Harrison Limited, Montreal, Canada.
[2]*Monsanto Canada Limited.*
[3]*Ayerst, McKenna and Harrison Limited.*

number of dialkylaminoethyl esters of the 2-(carboxyalkylamino)-2-imidazolines also have been prepared. These are described fully in the Experimental section.

The ethyl esters of the 2-(carboxyalkylamino)-2-imidazolines are converted into the corresponding amides (IV) by refluxing with amines in the presence of inert solvents. The amides are very difficult to purify as free bases. They are generally waxy light brown solids, so their dipicrates have been prepared for identification.

EXPERIMENTAL[4]

γ-Aminobutyric Acid

A solution of 2-pyrrolidone[5] (212.5 gm., 2.50 mole) and anhydrous barium hydroxide (223.3 gm., 1.30 mole) in 1 liter of water was heated at 100°C. for two hours. The solution was cooled, a few drops of concentrated hydrochloric acid added, and the solution was neutralized with 2.3 *N* sulphuric acid (1129 cc.). The suspension was boiled for 30 min. and then allowed to stand overnight. The barium sulphate was filtered (with the aid of Celite) and the filtrate, on evaporation, gave 200 gm. (78%) of crude product. One crystallization from ethyl alcohol (2 liters) yielded 170 gm. (68%) of product melting at 198–198.5°C.

ε-Aminocaproic Acid

A solution of ε-caprolactam[6] (113 gm., 1.0 mole) and anhydrous barium hydroxide (95.0 gm., 0.55 mole) in 1500 cc. water was heated at 100°C. for two hours. The solution was cooled, a few drops of concentrated hydrochloric acid were added, and the solution was neutralized by dropwise addition of 3 *N* sulphuric acid (370 cc.). The suspension of barium sulphate was boiled for 10 min., and then allowed to settle overnight. The precipitate was removed by filtration and the filtrate was evaporated, yield 120 gm. (92%). This crude residue was crystallized from ethyl alcohol (1 liter) to give 100 gm. (76.5%) of material melting at 200–202°C.

2-(γ-Carboxypropylamino)-2-imidazoline

Method A

A solution of 2-methylmercapto-2-imidazolinium iodide (1) (244 gm., 1.0 mole), γ-aminobutyric acid (98.0 gm., 0.95 mole), and sodium hydroxide (80 gm., 2.0 mole) in 2 liters of water was allowed to stand at room temperature for three days. The evolved methyl mercaptan was absorbed in 20% sodium hydroxide solution. At the end of the reaction period, the solution was diluted to a volume of 6 liters with water and it was passed through a column of mixed-bed resin (2 liters of Amberlite IRA–400[7] activated resin and 2 liters of Amberlite IRC-50 resin[7]) at a rate of 20 cc. per min. The column was washed with water and the combined eluate and washings were evaporataed *in vacuo*. The semicrystalline residue weighed 130 gm. (80% yield). Crystallization from methanol (300 cc.) gave 100 gm. of white crystals melting at 185–224°C.

[4]*All melting points are uncorrected. Microanalyses by C. W. Beazley, Skokie, Illinois, and Drs. Weiler and Strauss, Oxford, England.*
[5]*General Aniline and Film Corp., New York, N.Y.*
[6]*Dupont Co. of Canada Limited, Montreal, Que.*
[7]*Rohm and Haas Company, Philadelphia, Penn., U.S.A.*

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Another crystallization from methanol raised the melting point to a constant value of 224–225°C. Calc. for $C_7H_{13}N_3O_2$: C, 49.10; H, 7.65; N, 24.52%. Found: C, 48.78; H, 7.99; N, 24.75%. Its picrate, which was formed in aqueous solution, melted at 171–172°C. after crystallization from alcohol. Calc. for $C_{13}H_{16}N_6O_9$: C, 38.99; H, 4.03; N, 21.00%. Found: C, 38.79; H, 3.88; N, 21.18%.

Method B

A solution of 2-methylmercapto-2-imidazolinium iodide (122 gm., 0.5 mole) in 500 cc. of water was passed through a column of Amberlite IRA–400 resin (1 liter) at a rate of 7 cc. per min. and then the column was washed with 2 liters of water. γ-Aminobutyric acid (50.0 gm., 0.49 mole) was added to the total eluate and the solution was allowed to stand in the fume-hood at room temperature for 60 hr. An amorphous residue (79 gm., 95% yield)was obtained from evaporation of this solution *in vacuo*. One crystallization from methanol (200 cc.) gave pure 2-(γ-carboxypropylamino)-2-imidazoline (m.p. 224–225°C.). This product did not depress the melting point of a sample of the acid prepared by method A. The methanolic mother liquor on evaporation gave 12 gm. of oily residue. This oil has not been identified.

Method C

2-Methylmercapto-2-imidazolinium iodide (24.4 gm., 0.10 mole) was added to a solution of potassium hydroxide (11.4 gm., 0.20 mole) in 12 cc. of water. This solution was extracted with ether (4×50 cc.) and the ethereal solution was evaporated. Nine grams (77.5%) of the free base, 2-methylmercapto-2-imidazoline, was obtained. The 2-methylmercapto-2-imidazoline and γ-aminobutyric acid (7.5 gm., 0.073 mole) in methanol (100 cc.) were refluxed for two hours until the evolution of methylmercaptan had ceased. When the solution was concentrated *in vacuo*, 12 gm. (96% yield based on γ-aminobutyric acid) of 2-(γ-carboxypropylamino)-2-imidazoline (m.p. 223–225°C.) was obtained.

1-(β-Hydroxyethyl)-2-(γ-carboxypropylamino)-2-imidazoline

γ-Aminobutyric acid (64.3 gm., 0.62 mole), 1-(β-hydroxyethyl)-2-methylmercapto-2-imidazolinium iodide (4) (179.4 gm., 0.60 mole), and sodium hydroxide (25.0 gm., 0.62 mole) were dissolved in 3 liters of water and this solution was allowed to stand at room temperature for three days. After the reaction was complete, the solution was processed as described in method A above for 2-(γ-carboxypropyl)-2-imidazoline. The crude product (94 gm., 77% yield) was purified to constant melting point of 204.5–205.5°C. by crystallization from methanol, yield 36.0 gm. Calc. for $C_9H_{17}N_3O_3$: C, 50.22; H, 7.97; N, 19.53%. Found: C, 50.21; H, 8.12; N, 19.80%.

1-(β-Hydroxyethyl)-2-(ε-carboxypentylamino)-2-imidazoline

1-(β-Hydroxyethyl)-2-methylmercapto-2-imidazolinium iodide (115.2 gm., 0.40 mole) in 62 cc. of absolute ethanol was added to a 2.42 *N* absolute ethanolic potassium hydroxide solution at 0°C. Ether (680 cc.) was added and the precipitated potassium iodide (65.3 gm., 98.2% yield) was removed by filtration. ε-Aminocaproic acid (46 gm., 0.35 mole) was added to the filtrate and the ether was removed by distillation. The residual alcoholic solution was refluxed for six hours until the evolution of methylmercaptan ceased. The alcoholic

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solution on cooling gave 66.2 gm. (78%) of crude product which melted at 188–195°C. Crystallization from methanol (6 cc. per gm.) raised the melting point to a constant value of 209–210°C. Calc. for $C_{11}H_{21}N_3O_3$: C, 54.20; H, 8.70; N, 17.28%. Found: C, 54.25; H, 8.76; N, 16.80%.

2-(γ-Carbethoxypropylamino)-2-imidazoline

A solution of 2-(γ-carboxypropylamino)-2-imidazoline (17.1 gm., 0.1 mole) in ethanol (150 cc.) containing 0.3 mole of hydrogen chloride was refluxed for two hours. Benzene (50 cc.) was added and the refluxing was continued another hour. The benzene was distilled from the solution to remove water as the benzene–water–alcohol azeotrope. This procedure was repeated twice more and then the solution was taken to dryness, yield 21.0 gm. (89.5%). A sample of this product in aqueous solution was converted into its picrate. Its melting point was raised from 104–108°C. to 114–115°C. by three crystallizations from 50% aqueous ethanol. Calc. for $C_{15}H_{20}N_6O_9$: C, 42.02; H, 4.71; N, 19.62%. Found: C, 42.19; H, 4.65; N, 19.9%.

2-(N-γ-Dimethylaminopropyl-γ-carbamylpropylamino)-2-imidazoline

The above-described 2-(γ-carbethoxypropylamino)-2-imidazolinium chloride (20.5 gm., 0.087 mole) and γ-dimethylaminopropylamine (10.4 gm., 0.1 mole) were dissolved in absolute ethanol (200 cc.) and this solution was refluxed for four hours. Then the solution was evaporated to dryness and the residue was dissolved in 300 cc. of water. This aqueous solution was passed through a column of activated Amberlite IRA-400 resin (400 cc.) and the column was washed with water (1 liter). On evaporation the eluate gave 5.5 gm. (24.7%) of a brown gummy solid. This solid, its mono- and its di-hydrochlorides, could not be purified by crystallization. Its picrate formed from aqueous solution melted at 155–155.5°C. Calc. for $C_{24}H_{31}N_{11}O_{15}$: C, 40.38; H, 4.38; N, 21.6%. Found: C, 40.37; H, 4.56; N, 21.82%.

β-Diethylaminoethylamine

N,N-Diethyl ethylenediamine (b.p. 146–150°C. at 760 mm.; $n_D^{25} = 1.4345$) was obtained in 41% yield by the method of Braz and Skorodumov (2). This reaction also gave a 21.8% yield of N,N-diethyl-N′-(2-aminoethyl) ethylenediamine ($n_D^{27} = 1.4572$) as well as higher addition products.

2-(N-β-Diethylaminoethyl-γ-carbamylpropylamino)-2-imidazoline

A solution of 2-(β-carbethoxyethylamino)-2-imidazolinium chloride (7.34 gm., 0.029 mole) and β-diethylaminoethylamine (3.4 gm., 0.029 mole) in 60 cc. of absolute ethanol was refluxed for four hours. After evaporation, this solution gave 9.0 gm. (95%) of amorphous material. The residue was dissolved in methanol (100 cc.) and the methanolic solution was passed through a column of Amberlite IRA-400 resin (150 cc.). After the column was washed with methanol (450 cc.), the total eluate was evaporated. The oily residue weighed 3.2 gm. (35.6%). It could be crystallized from ethyl acetate (8 cc.) to give a gummy reddish solid. A picrate formed from this solid melted at 135–135.5°C. Calc. for $C_{25}H_{33}N_{11}O_{15}$: C, 41.26; H, 4.57; N, 21.2%. Found: C, 41.11; H, 4.36; N, 21.28%.

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2-(N-γ-Dimethylaminopropylcarbamylmethylamino)-2-imidazoline (VI)

2-(Carbethoxymethylamino)-Δ^2-1,3-diazacyclopentene hydrochloride (3) (4.23 gm., 0.02 mole) and 2.08 gm. (0.02 mole) of N,N-dimethylaminopropylamine were refluxed in the presence of 40 cc. of absolute ethanol for four hours. On cooling in the refrigerator, a white solid separated, yield 0.658 gm. (22.5%). This solid melted at 280°C. with decomposition. It was identified as the free acid 2-(carboxymethylamino)-Δ^2-1,3-diazacyclopentene, by a comparison of their infrared absorption spectra. The ethanolic filtrate from the free acid was taken to dryness *in vacuo*. The residue was a viscous oil, which crystallized on standing, yield 4.09 gm. (74.8% as the monohydrochloride). A small sample of this solid was precipitated as its picrate from its aqueous solution. Two crystallizations from water raised the melting point from 167°C. to 189.5–191°C. Anal. Calc. for dipicrate $C_{22}H_{27}N_{11}O_{15}$: C, 38.52; H, 3.97; N, 22.48%. Found: C, 38.11; H, 4.14; N, 22.25%.

Dimethylaminoethyl Ester of 2-(ε-Carboxypentylamino)-2-imidazolinium Chloride Monopicrate

2-(ε-Carboxypentylamino)-2-imidazoline (3) (9.9 gm., 0.05 mole) and dimethylaminoethanol (4.5 gm., 0.05 mole) were suspended in 150 cc. of toluene and heated at 140°C. for 10 hr. During the heating period dry hydrogen chloride was bubbled through the solution and toluene was distilled over slowly. Fresh toluene was added at intervals as required. On cooling, the toluene was decanted and the oily residue was converted into its picrate in aqueous solution, yield 17 gm. (63.5%). The melting point of this picrate was raised from 183–185°C. to 186–187.5°C. by one crystallization from ethanol. Calc. for $C_{19}H_{30}ClN_7O_9$: C, 42.65; H, 5.63; Cl, 6.62; N, 18.30%. Found: C, 43.02; H, 5.57; Cl, 6.75; N, 18.28%.

Dimethylaminoethyl Ester of 2-(γ-Carboxypropylamino)-2-imidazolinium Chloride Monopicrate

The dimethylaminoethyl ester of 2-(γ-carboxypropylamino)-2-imidazoline chloride monopicrate (m.p. 183–185°C.) was prepared in 46.3% yield by the above procedure. One crystallization from acetonitrile raised the melting point to a constant value of 188–189°C. Calc. for $C_{17}H_{26}ClN_7O_9$: C, 40.25; H, 5.16; Cl, 6.98; N, 19.35%. Found: C, 40.44; H, 5.15; Cl, 6.73; N, 19.25%.

Dimethylaminoethyl Ester of 2-(Carboxymethylamino)-2-imidazoline Dipicrate

The above esterification procedure gave the dipicrate of the dimethylaminoethyl ester of 2-(carboxymethylamino)-2-imidazoline (m.p. 152–156°C.) in 48.0% yield. Two crystallizations from acetonitrile raised the melting point to 161.5–165.5°C. Calc. for $C_{21}H_{24}N_{10}O_{16}$: C, 37.55; H, 3.37; N, 20.85%. Found: C, 37.85; H, 3.46; N, 20.57%.

In a similar manner the following dialkylaminoalkyl esters of 2-(ε-carboxypentylamino)-2-imidazoline were prepared.

Diisopropylaminoethyl Ester of 2-(ε-Carboxypentylamino)-2-imidazoline Dipicrate

M.p. 127–130°C.; yield 86.6%. Calc. for $C_{29}H_{40}N_{10}O_{16}$: C, 44.35; H, 5.14; N, 17.85%. Found: C, 44.76; H, 5.08; N, 17.78%.

Diethylaminoethyl Ester of 2-(ε-Carboxypentylamino)-2-imidazoline Dipicrate

M.p. 120–123°C.; yield 68.8%. Calc. for $C_{27}H_{36}N_{10}O_{16}$: C, 42.85; H, 4.79; N, 18.51%. Found: C, 43.15; H, 4.51; N, 18.49%.

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THE DISTRIBUTION OF PLUTONIUM IN THE SYSTEMS URANIUM–SILVER AND URANIUM–SILVER–GOLD[1]

By D. E. McKenzie

ABSTRACT

An expression due to Hildebrand and Scott has been used to select silver as a possible extractant for plutonium from neutron-irradiated uranium. The distribution of plutonium between molten silver and molten neutron-irradiated uranium has been examined in small-scale experiments. The fraction of plutonium in the silver layer increases with increasing temperature. For equal weights of silver and uranium containing 0.1% plutonium, 88% of the total plutonium is distributed to the silver phase at 1350°C. Greater proportions of plutonium are found in the silver phase in experiments with uranium of lower initial plutonium concentration. On the addition of gold to the system plutonium extraction is increased and passes through a maximum. This maximum appears to be associated with a particular concentration of gold in silver and of gold in uranium.

INTRODUCTION

A cheap and simple method for the separation of plutonium from neutron-irradiated uranium may be important to the development of cheap nuclear power. One approach of some promise for metallic uranium fuels is to achieve the separation while retaining the uranium as metal. The volatilization of plutonium from neutron-irradiated uranium was described in a previous paper (3) as an example of this approach. A second possible technique makes use of the principle of molten metal extraction. In this method plutonium is extracted from molten uranium into a metal which is essentially immiscible with uranium. As the extracting metal, silver has shown considerable promise. The theoretical background used for the selection of silver and some of the results obtained with this metal are described in this paper. The use of silver has also been considered by Dr. F. H. Spedding and co-workers at the Ames laboratory of the United States Atomic Energy Commission. Recent work by this group was reported at Geneva, Switzerland, in August, 1955 (7).

SELECTION OF AN EXTRACTING METAL

For the extraction of plutonium from uranium, a metal was required which dissolved plutonium but which was essentially immiscible with uranium. Although uranium phase diagrams were available, a theoretical method was required to predict which metals would dissolve plutonium.

A method due to Hildebrand and Scott (2, p. 333) was used. They deduced as a criterion for the complete miscibility of two liquid metals the expression

$$\tfrac{1}{2}(V_1+V_2)(\delta_1-\delta_2)^2 < 2RT,$$

where V_1 and V_2 are the atomic volumes of metals 1 and 2,

δ_1 and δ_2 are the solubility parameters of 1 and 2,

R is the gas constant and T is the absolute temperature.

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The solubility parameter δ is given by the expression $\delta = (\Delta E_v/V)^{\frac{1}{2}}$ where ΔE_v is the energy of vaporization of the metal. Hildebrand and Scott have calculated the solubility parameters of most metals (2, p. 323). For plutonium a value for δ of 84 at room temperature was determined from the available data.

The miscibility criterion was used to compile a group of metals whose liquids should be miscible with liquid plutonium. From this group were chosen those metals which were immiscible with liquid uranium and which would exist as liquids under one atmosphere pressure in the temperature range 1132° to 1400°C. In this manner silver and the rare earth metals were predicted as possible extracting agents. Of these, silver appeared the most promising because its physical and chemical properties are so markedly different from those of plutonium.

EXPERIMENTAL

Materials and Apparatus

The neutron-irradiated uranium was cut from rods which had been irradiated in the NRX reactor and allowed to decay for three years. For each experiment the uranium was washed immediately before use in dilute nitric acid, water, and then acetone. The silver with a fineness of 999.7 was obtained from the Royal Canadian Mint. Beryllia crucibles were purchased from the Brush Beryllium Co.

Molten uranium and molten silver were contacted in a bell jar type of apparatus which is illustrated in Fig. 1. Cooling water was circulated through a copper coil soldered around the mild steel bell and through a compartment

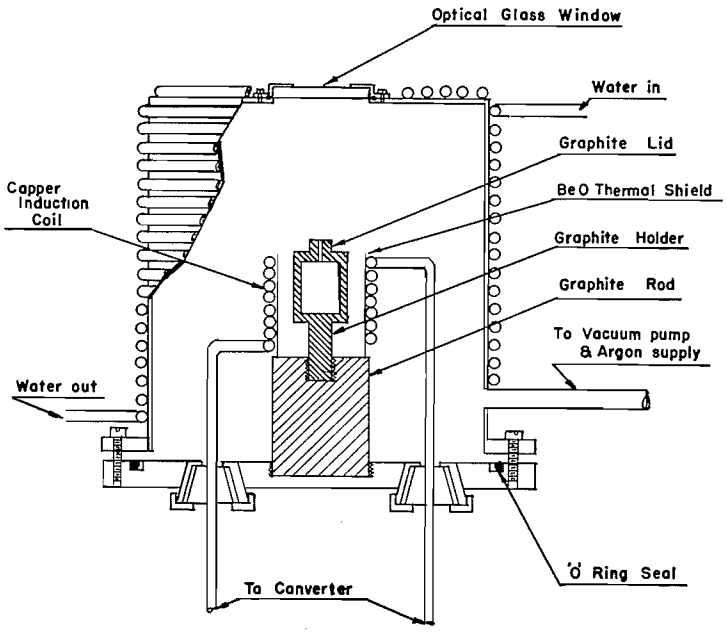

FIG. 1. Diagram of apparatus for contacting uranium and silver.

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in the fixed bottom plate. Heat was supplied by a 15 kva. Lepel sparkgap induction furnace. The chamber was evacuated by a Welch Duo-seal mechanical pump and welding grade argon was used as an inert atmosphere. The bell jar resided in a lead-shielded dry box and was viewed through high density glass.

Temperatures were determined with an optical pyrometer. The pyrometer was calibrated from observations of the melting of various solids of known melting point in the apparatus. A rough check of the calibration was obtained by observing the melting point of silver in each run. The temperatures have a probable error of ±25°C.

A different apparatus which will be described in a later communication was used to determine the temperature coefficient of plutonium distribution. The charge was resistance heated and its temperature measured by a thermocouple. The temperatures cited for these measurements are accurate to ±5°C.

Procedures and Analyses

For an experiment weighed amounts of silver and neutron-irradiated uranium in a beryllia crucible were placed in the graphite holder, the bell bolted to the bottom plate, and the chamber evacuated to a pressure of 1 to 10 microns of Hg. The pump was then diverted and the chamber filled to atmospheric pressure with argon. The evacuation and argon filling were repeated three times before heating. The charge was held at temperature for 20 min., which was found to be ample time to establish equilibrium.

After cooling in argon, the metal billet was removed from the crucible and placed in dilute hydrochloric acid to remove the uranium phase. The silver phase which remained was washed thoroughly with water, dried, and weighed. It contained substantially all of the original silver and about 5% by weight of uranium, in approximate agreement with published solubility data (1). This phase was dissolved in dilute nitric acid. In runs in which gold was added, a fluffy black residue, containing most of the gold in the silver layer, remained and was dissolved in aqua regia.

The solutions were analyzed for plutonium by standard radiochemical procedures and the distribution coefficient K_{Pu} calculated where K_{Pu} = mole fraction of plutonium in silver/mole fraction of plutonium in uranium. Gold analyses were performed using the iodide method (5) and K_{Au} calculated from K_{Au} = mole fraction of gold in silver/mole fraction of gold in uranium.

RESULTS AND DISCUSSION

Variation of K_{Pu} with Temperature

The temperature range of interest in this system lies between 1132°C., the melting point of uranium, and 1350°C., above which temperature silver begins to distill at an appreciable rate in one atmosphere of argon. K_{Pu} increases with temperature in this range. The results are summarized in Table I and plotted as log K_{Pu} vs. $1/T$ in Fig. 2.

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TABLE I

VARIATION OF K_{Pu} WITH TEMPERATURE

U/Ag weight ratio = 1/1, initial Pu concentration = 0.10±.01%

Run No.	Temp. (°C.)	Wt. U (gm.)	K_{Pu}
B10	1160	3.6345	2.01
B9	1200	4.1647	2.27
B8	1250	3.9676	2.62
B11	1300	3.6350	2.93
B12	1350	3.7455	3.31
B7	1350	4.4005	3.45

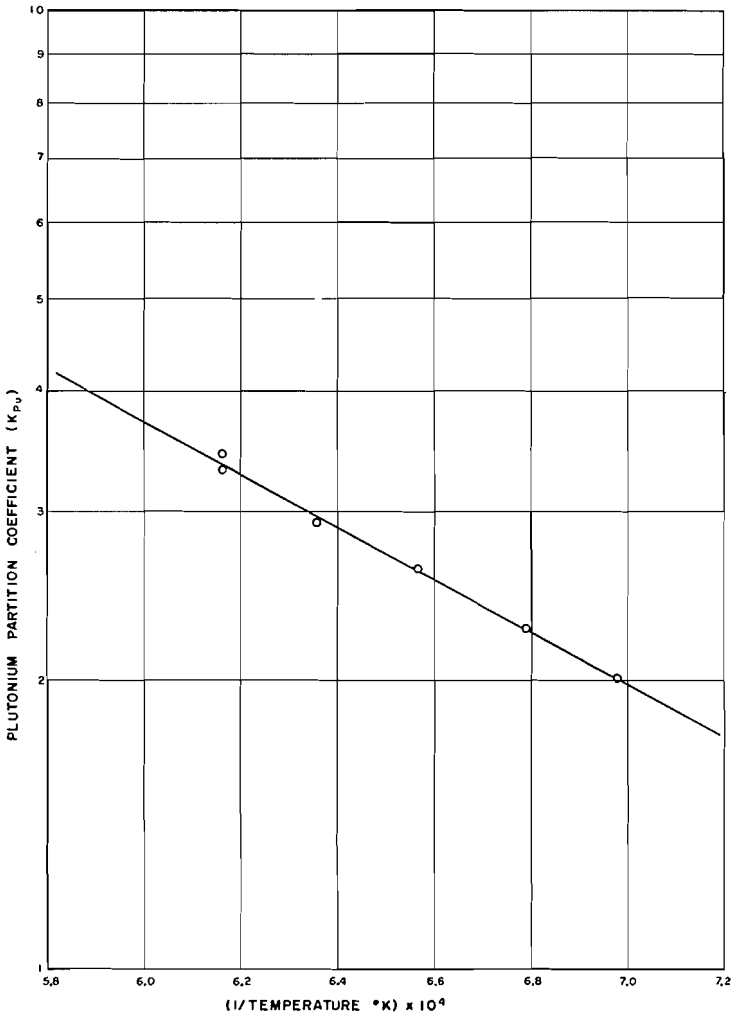

FIG. 2. The variation of K_{Pu} with temperature. U/Ag weight ratio = 1/1. Initial plutonium concentration in uranium = 0.1±0.01%.

The data have been treated by the least squares method to give the equation $\log K_{Pu} = 2.21 - 2.74 \times 10^3/T$. A value for ΔH of 12.5 kcal. is obtained from

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the slope of this line. (The uncertainties in a single determination of K_{Pu} are equivalent to an error of ± 0.5 kcal. in ΔH.) This ΔH represents the heat of transfer of one gram-atom of plutonium from liquid uranium to liquid silver and, hence, is the sum of a total or integral heat of solution of plutonium in silver and a heat of dilution of plutonium in neutron-irradiated uranium. From investigations of the volatilization of plutonium from uranium fuel (3, 4) it was concluded that plutonium behaves essentially ideally in molten neutron-irradiated uranium in the temperature range 1540–1770°C. This conclusion implies a zero heat effect associated with the removal of plutonium from this material at such temperatures. Assuming the validity of this conclusion and that ideal behavior extends to the lower temperatures encountered in the present work, the measured heat of transfer is a total heat of solution, per gram-atom of plutonium, of liquid plutonium in liquid silver. Recognizing that the equilibrium concentration of plutonium in silver is about 0.05 atom %, 12.5 kcal. may be considered as $\bar{L}^{\circ}_{Pu}$, the limiting partial molal heat content, relative to liquid plutonium, of plutonium in liquid silver, or "the partial molar heat of mixing of plutonium in silver" (6).

Variation of K_{Pu} with Plutonium Concentration

Plutonium concentrations were varied by choosing uranium of suitable irradiation history and also by adding natural uranium as required. K_{Pu} was found to increase with decreasing plutonium concentration. The data are given in Table II and plotted as log K_{Pu} vs. log(Pu concentration) in Fig. 3. Included in the data is a value for K_{Pu} at 1325°C. and an initial plutonium concentration of 0.1%, calculated from the equation derived in the preceding section.

TABLE II

VARIATION OF K_{Pu} WITH PLUTONIUM CONCENTRATION
U/Ag weight ratio = 1/1, temperature = 1325±25°C.

Run No.	Wt. U (gm.)	Initial Pu conc. in U (%)	K_{Pu}
61	8.823	3.63×10^{-4}	7.48
72	5.852	5.08×10^{-4}	6.87
60	4.631	8.29×10^{-4}	5.93
71	5.642	2.21×10^{-3}	6.58
70	4.113	5.22×10^{-3}	5.16
79	3.847	8.50×10^{-3}	5.31
119	5.408	4.24×10^{-2}	4.20
—	—	1.0×10^{-1}	3.16

The equation $\log K_{Pu} = 0.47 - 0.11 \log(\text{initial \% Pu in U})$ describes approximately the increase in plutonium extraction with decreasing plutonium concentration. In the recent work with silver at the Ames laboratory (7) a similar effect was observed in extractions from uranium/chromium alloy but the opposite effect, i.e. a decrease in extraction with decreasing plutonium concentration, was obtained for extractions from uranium. The latter results, which were obtained at 1200 °C. using samples of uranium of two different plutonium concentrations, are also plotted in Fig. 3.

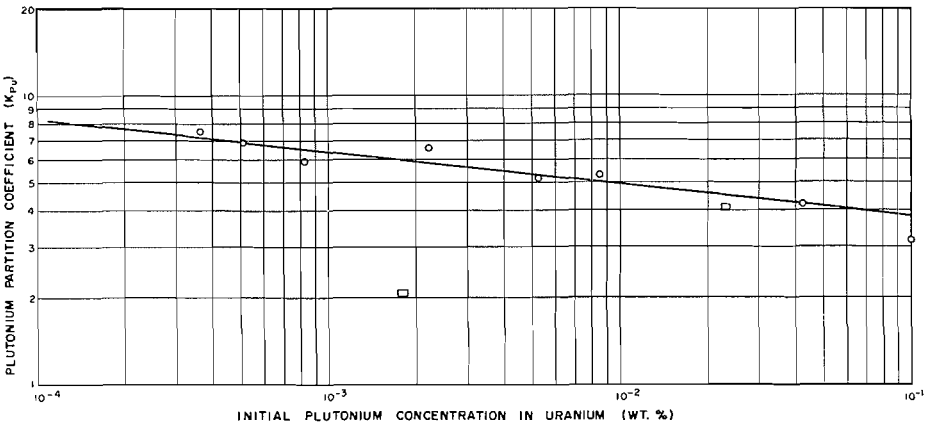

FIG. 3. The variation of K_{Pu} with plutonium concentration.
○ This work. U/Ag weight ratio = 1/1. Temperature 1325±25°C.
□ Voigt's (7) results. U/Ag weight ratio = 1.8/1. Temperature = 1200°C.

Variation of K_{Pu} with the Addition of Gold to the Uranium/Silver System

The effect, on plutonium distribution, of adding other metals to the uranium/silver system was examined for effects analogous to those of complexing or salting-out agents in water/organic solvent systems. The metal was added to a silver and uranium charge and then the melting and contacting operations performed. The metals cerium, tin, gold, copper, magnesium, lead, bismuth, aluminum, lithium, and gallium were considered but all, except gold, showed an adverse effect on plutonium extraction. In each case the weight of the added metal was less than 4% of the weight of uranium in the run.

The extraction of plutonium by silver/gold alloys was studied in greater detail. The extraction exhibits a dependence on gold concentration whereby K_{Pu} passes through a maximum. Also, the distribution of gold between uran-

TABLE III

VARIATION OF K_{Pu} ON THE ADDITION OF GOLD
U/Ag weight ratio = 1/1, initial Pu concentration = 0.01±0.0015%, temperature = 1325±25°C.

Run No.	Wt. U (gm.)	Au added (wt.% of U)	K_{Pu}	K_{Au}*
79	3.847	—	5.31	—
104	4.805	0.69	7.50	—
80	5.170	1.44	5.21	2.56
81	3.984	2.03	4.94	—
82	3.497	2.37	7.54	2.56
83	3.961	2.53	6.31	—
84	4.971	2.91	9.65	2.49
85	5.522	3.23	12.9	2.72
86	4.566	3.75	12.2	2.42
94	4.182	4.02	5.57	—
95	5.528	4.36	7.04	2.26
106	3.688	4.73	4.35	—

**The distribution of gold was not determined for all runs.*

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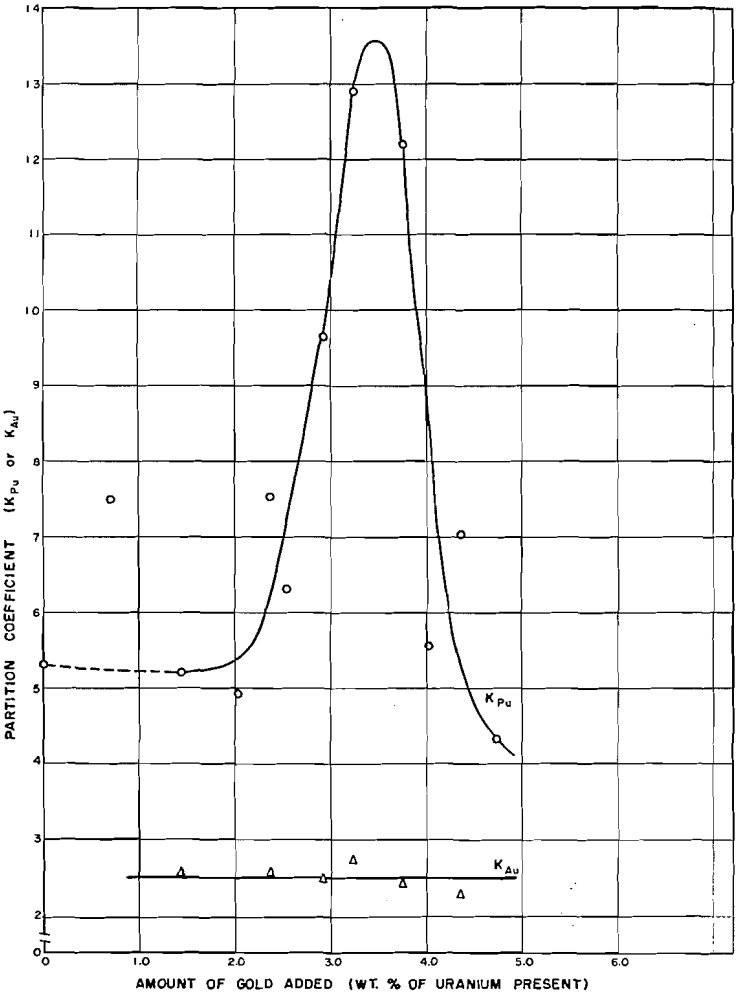

FIG. 4. The variation of K_{Pu} with gold additions. U/Ag weight ratio = 1/1. Temperature = 1325±25°C. Initial plutonium concentration in uranium = 0.01±0.0015%.

ium and silver has been determined and K_{Au}, for a given uranium to silver ratio, appears to be independent of the amount of gold added. A typical set of data is shown in Table III which summarizes the results for a uranium to silver ratio of 1/1. These results are plotted as K_{Pu} vs. Au concentration in Fig. 4. For this ratio a maximum value for K_{Pu} of about 13.5 is obtained, corresponding to a gold addition of 3.5 wt. % of the uranium present.

Similar studies have been made for uranium to silver weight ratios of 2/1, 4/1, and 8/1 at the same temperature (1325°C.) and using uranium of the same initial plutonium concentration (0.01%). The maximum values of K_{Pu} were essentially the same as that found for a 1/1 ratio of uranium to silver. However, maximum plutonium extraction occurs at a different amount of added gold

for each ratio. The gold addition corresponding to maximum K_{Pu} and the average K_{Au} for each ratio are presented in columns 2 and 3 of Table IV. By combining these data, the concentration of gold in silver and in uranium may be calculated for the condition of maximum K_{Pu}. The results of the calculations are shown in columns 5 and 7 of Table IV. It appears that, within the precision of the data, maximum plutonium extraction is achieved at essentially a uniform concentration of gold in silver and also a uniform concentration of gold in uranium independent of the uranium to silver ratio.

TABLE IV

GOLD CONCENTRATIONS IN URANIUM AND IN SILVER FOR MAXIMUM VALUES OF K_{Pu}
Initial Pu concentration = 0.01±0.0015%, temperature = 1325±25°C.

U/Ag ratio (by wt.)	Au addition for max. K_{Pu} (wt.% of U)	K_{Au}	% added Au in U at equil.	Equil. Au conc. in U (wt.%)	% added Au in Ag at equil.	Equil. Au conc. in Ag (wt.%)
1/1	3.5	2.50	15.4	0.5	84.6	3.0
2/1	1.5	1.74	34.1	0.5	65.9	2.0
4/1	1.5	1.77	50.6	0.8	49.4	3.0
8/1	1.0	1.8	66	0.7	34	2.7

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THE PREPARATION AND SOME CLEAVAGE REACTIONS OF ALKYL AND SUBSTITUTED ALKYL METHANESULPHONATES

THE SYNTHESIS OF FLUORIDES, IODIDES, AND THIOCYANATES[1,2]

By F. L. M. Pattison and J. E. Millington

ABSTRACT

Representative esters of methanesulphonic acid were synthesized, and cleaved to form the corresponding fluorides, iodides, and thiocyanates. From this work was developed a convenient laboratory procedure for converting alcohols to fluorides.

The preparation and uses of simple alkyl sulphonates, $ROSO_2R'$, have received considerable attention (7, 8, 9, 10, 26, 27, 30), but little information is available on the reactions of those alkyl sulphonates in which R contains a second functional group. The work described in this paper was undertaken with two objectives: (*a*) to develop a new method of preparing ω-fluoroalkyl compounds, which in turn were required for toxicity studies (20, 21), and (*b*) to examine the reactivity of the sulphonate group relative to that of other functional groups in the same molecule. Methanesulphonates were investigated in most detail, but some benzenesulphonates and *p*-toluenesulphonates were prepared and used for comparison studies on the relative reactivities of the sulphonate moieties.

The sulphonates were prepared by three methods. (1) Esterification of alcohols with the appropriate sulphonyl chloride (19, 26) or fluoride (21) was found to be convenient and economical. Results are summarized in Table I. (2) Occasionally, treatment of iodides or bromides with silver methanesulphonate in acetonitrile (10) proved to be satisfactory, particularly in those instances in which the corresponding hydroxyl compounds were unstable or inaccessible. Results are summarized in Table II. (3) Early in the work, a new method was developed for the preparation of ω-chloroalkyl methanesulphonates by opening of cyclic ethers with methanesulphonyl chloride; an analogous method has subsequently been reported for the preparation of 4-chlorobutyl *p*-toluenesulphonate (11). Conditions and yields are summarized in Table III. One reaction using benzenesulphonyl chloride was carried out: the acid chloride, ethylene oxide, and a trace of zinc chloride were sealed in a glass ampoule and allowed to stand at room temperature for 70 days; 2-chloroethyl benzenesulphonate was obtained in 82% yield.

(1) $ROH + XSO_2R' \rightarrow ROSO_2R' + HX \quad (X = F \text{ or } Cl)$

(2) $RX + AgOSO_2R' \rightarrow ROSO_2R' + AgX \quad (X = Br \text{ or } I)$

(3) $(CH_2)_nO + MsCl \rightarrow Cl(CH_2)_nOMs$

[1]*Manuscript received January 31, 1956.*
Contribution from the Department of Chemistry, University of Western Ontario, London, Canada. Issued as D.R.B. Report No. SW-18.

[2]*To avoid ambiguity, fluorine is not referred to as halogen throughout this report.*
Ms = $CH_3SO_2^-$; *Bs* = $C_6H_5SO_2^-$; *Ts* = *p*-$CH_3C_6H_4SO_2^-$.

Physical constants of the sulphonates prepared by the above methods are listed in Table IV.

TABLE I

PREPARATION OF METHANE-, BENZENE-, AND *p*-TOLUENE-SULPHONATES FROM ALCOHOLS

Product	Alcohol	MsCl, mole	MsF, mole	BsCl, mole	TsCl, mole	Base	Mole	Temp., °C.	Time, hr.	Yield, %
$Cl(CH_2)_2OMs$	$Cl(CH_2)_2OH$	1.0	0.22			NaOH	0.22	25	5.5	75
		0.5	0.1			KF	0.3	25	6	88
$Cl(CH_2)_2OBs$		0.94		0.94		C_5H_5N	1.1	−10	5	76
$Cl(CH_2)_2OTs$		1.25			0.5	NaOH	0.5	25	3.5	88
$Cl(CH_2)_3OMs$	$Cl(CH_2)_3OH$	0.75	0.75			C_5H_5N	1.0	− 3	3	83
$Cl(CH_2)_4OMs$	$Cl(CH_2)_4OH$	0.36	0.40			C_5H_5N	1.0	− 5	4	80
$Cl(CH_2)_5OMs$	$Cl(CH_2)_5OH$	0.23	0.24			C_5H_5N	1.0	−15	4	68
		0.21	0.21			NaOH	0.21	−10	4	12
$Br(CH_2)_2OMs$	$Br(CH_2)_2OH$	0.50	0.50			C_5H_5N	0.5	0	2	72
$MeO(CH_2)_2OMs$	$MeO(CH_2)_2OH$	0.30	0.30			C_5H_5N	1.2	0	5	30
$EtO(CH_2)_2OMs$	$EtO(CH_2)_2OH$	0.55	0.50			C_5H_5N	0.7	− 3	2.5	31
$CH_3(CH_2)_5OMs$	$CH_3(CH_2)_5OH$	0.50	0.50			C_5H_5N	0.75	−18	4	89
$CH_3(CH_2)_5OBs$		0.15		0.15		C_5H_5N	0.15	− 5	3.5	64
$CH_3(CH_2)_5OTs$		0.20			0.20	C_5H_5N	0.5	− 5	4	89
$(CH_3)_2CHCH_2OMs$	$(CH_3)_2CHCH_2OH$	0.20	0.20			C_5H_5N	0.63	− 4	3	76
		0.20	0.20			KF	0.30	104	6.5	16
$CH_2{:}CH(CH_2)_3OMs$	$CH_2{:}CH(CH_2)_3OH$	0.50	0.50			C_5H_5N	1.0	− 5	2.5	78.5

TABLE II

PREPARATION OF METHANESULPHONATES FROM HALIDES

Product	Halide	Mole	Silver methanesulphonate, mole	Yield, %
$MsOCH_2COOEt$	ICH_2COOEt	0.1	0.1	62
$MsOCH_2COCH_3$	$BrCH_2COCH_3$	0.2	0.2	43.5
$MsOCH_2CH{:}CHCOOEt$	$BrCH_2CH{:}CHCOOEt$	0.3	0.3	60
$MsOCH(COOEt)_2$	$BrCH(COOEt)_2$	0.1	0.1	47
$MsOCH_2CH(OEt)_2$	$BrCH_2CH(OEt)_2$	0.1	0.1	60

TABLE III

CONVERSION OF CYCLIC ETHERS TO ω-CHLOROALKYL METHANESULPHONATES

Cyclic ether	Moles	MsCl, mole	Temp., °C.	Time, hr.	Conversion, %	Yield, %
$(CH_2)_2O$	2.0	0.50	25	180	33	47
	1.5	0.51	40	32	35	50
	0.5	0.23	22	1680	22	46
$(CH_2)_4O$	0.33	0.33	80	4	26	69
	0.33	0.33	85	20	36	53

Reactions of Sulphonates with Potassium Fluoride (8, 21)

$$ROMs + KF \rightarrow RF + MsOK$$

Initially, replacement of the sulphonoxy group (CH_3SO_2O–) by fluoride was attempted in methanol; however, the isolation of a relatively large proportion

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TABLE IV

PHYSICAL CONSTANTS OF METHANE-, BENZENE-, AND *p*-TOLUENE-SULPHONATES

Compound	Boiling point		n_D^{25}	d_4^{20}
	°C.	mm.		
2-Chloroethyl methanesulphonate	130	11.5	1.4545	1.420
3-Chloropropyl methanesulphonate	143–146	9	1.4548	1.337
4-Chlorobutyl methanesulphonate	115	0.5	1.4570	1.272
5-Chloroamyl methanesulphonate	128	1	1.4581	1.236
2-Bromoethyl methanesulphonate	140–142	11	1.4805	1.703
2-Methoxyethyl methanesulphonate[a]	126	12	1.4308	
2-Ethoxyethyl methanesulphonate[b]	132–134	12	1.4303	
n-Hexyl methanesulphonate[c]	107–108	3.5	1.4324	
Isobutyl methanesulphonate[d]	99–101	11.5	1.4232	
Pent-4-enyl methanesulphonate	79–80	0.15	1.4444	1.123
Ethyl methanesulphonoxyacetate	148	9	1.4365	1.317
Methanesulphonoxyacetone	104	0.4	1.4445	1.305
Ethyl 4-methanesulphonoxycrotonate	120	0.2	1.4628	1.250
Diethyl methanesulphonoxymalonate	117	0.1	1.4400	1.292
Diethyl methanesulphonoxyacetal	82	0.15	1.4338	1.183
2-Chloroethyl benzenesulphonate[e]	139	2	1.5276	
n-Hexyl benzenesulphonate[f]	125	0.2	1.4952	
2-Chloroethyl *p*-toluenesulphonate[g]	142	1	1.5282	
n-Hexyl *p*-toluenesulphonate[h]	145	0.5	1.4968	

[a] *Chapman and Owen (4) report b.p. 80° at 0.4 mm. and* n_D^{20} *1.4314.*

[b] *Newman and Magerlein (19) report b.p. 122–124° at 7 mm. and* n_D^{25} *1.4303.*

[c] *Williams and Mosher (30) report b.p. 78° at 1 mm. and* n_D^{20} *1.4336.*

[d] *Williams and Mosher (30) report b.p. 53° at 1 mm. and* n_D^{20} *1.4245.*

[e] *Bert (2) reports b.p. 192° at 15 mm.*

[f] *Emling (9) reports b.p. 135–136° at 0.5 mm. and* n_D^{25} *1.4952.*

[g] *Tipson and Cretcher (29) report b.p. 140° at 1.5 mm. and* n_D^{25} *1.5280.*

[h] *Drahowzal and Klamann (7) report b.p. 149° et 0.5 mm. and* n_D^{20} *1.4996.*

of hexyl methyl ether from a mixture of potassium fluoride and hexyl methanesulphonate indicated the unfavorable properties of this solvent. Dimethyl formamide, dimethyl sulphoxide, and diethyl cellosolve were found to be unsuitable. Ethylene glycol gave results analogous to those obtained with methanol, but diethylene, triethylene, and tetraethylene glycols did not exhibit the same tendency for ether formation. Diethylene glycol was finally selected as the solvent for this study because of its availability and ease of purification. The product was continuously removed as the reaction proceeded. Conditions and yields are summarized in Table V.

The main side reactions were: (*a*) dehydration of diethylene glycol in the presence of potassium fluoride to give dioxane; and (*b*) replacement of halide by fluoride to give ω,ω'-difluoroalkanes. In all the cleavage reactions, appreciable quantities of dioxane were formed, and when temperatures higher than those listed in Table V were used, difluoroalkanes were obtained from ω-haloalkyl methanesulphonates in 40–60% yield.

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TABLE V

PREPARATION OF ALKYL AND SUBSTITUTED ALKYL FLUORIDES
(Molar scale: 0.1 mole methanesulphonate; 0.2–0.3 mole potassium fluoride, *ca.* 200 gm. solvent)

Product	Methanesulphonate	Solvent[a]	Time, hr.	Temp., °C.	Press., mm.	Yield, %
$CH_3(CH_2)_5F$	$CH_3(CH_2)_5OMs$	MeOH	17	66	750	9
		MeOH	17	95	—	0
		E.G.	4	100	300	10
		D.G.	9	105	750	18
		D.G.	4	100	300	67
		Tri E.G.	4	100	300	52[b]
		Tetra E.G.	4	100	300	50[b]
		D.G.	4	100	300	50[b]
$Cl(CH_2)_2F$	$Cl(CH_2)_2OMs$	MeOH	11.5	66	740	49
		D.G.	4.5	100	300	73
$Cl(CH_2)_3F$	$Cl(CH_2)_3OMs$	D.G.	4	100	320	65
$Cl(CH_2)_4F$	$Cl(CH_2)_4OMs$	D.G.	4.5	100	220	64
$Cl(CH_2)_5F$	$Cl(CH_2)_5OMs$	D.G.	4.5	100	70	66
$Br(CH_2)_2F$	$Br(CH_2)_2OMs$	D.G.	4.5	125	280	20
		D.G.	4	100	300	67
$MeO(CH_2)_2F$	$MeO(CH_2)_2OMs$	D.G.	4	100	300	75
$EtO(CH_2)_2F$	$EtO(CH_2)_2OMs$	D.G.	4	100	300	68
$CH_2{:}CH(CH_2)_3F$	$CH_2{:}CH(CH_2)_3OMs$	D.G.	2.2	100	450	36.5
FCH_2COOEt	$MsOCH_2COOEt$	D.G.	2	100	340	47
FCH_2COCH_3	$MsOCH_2COCH_3$	D.G.	1.5	100	320	50
$FCH_2CH{:}CHCOOEt$	$MsOCH_2CH{:}CHCOOEt$	D.G.	3	100	13	50
$FCH(COOEt)_2$	$MsOCH(COOEt)_2$	D.G.	3.5	100	17	0
$FCH_2CH(OEt)_2$	$MsOCH_2CH(OEt)_2$	D.G.	2.5	100	75	0

[a]*E.G. = Ethylene glycol. D.G. = Diethylene glycol. Tri E.G. = Triethylene glycol. Tetra E.G. = Tetraethylene glycol.*
[b]*Carried out using 0.05 mole of methanesulphonate.*

A number of reactions were carried out by the same procedure and under the same conditions as described above, in order to determine the relative reactivities of the sulphonate moieties. The results, shown in Table VI, do not exhibit any characteristic trend.

TABLE VI

INFLUENCE OF THE SULPHONATE MOIETY
(Molar scale: 0.1 mole sulphonate; 0.2–0.3 mole potassium fluoride; *ca.* 200 gm. solvent)

Product	Sulphonate	Solvent	Temp., °C.	Press., mm.	Yield, %
$Cl(CH_2)_2F$	$Cl(CH_2)_2OMs$	MeOH	66	740	49
	$Cl(CH_2)_2OBs$	MeOH	66	740	60
	$Cl(CH_2)_2OTs$	MeOH	66	740	0
		MeOH	95	—	25
	$Cl(CH_2)_2OMs$	D.G.	100	300	73
	$Cl(CH_2)_2OBs$	D.G.	100	300	77
	$Cl(CH_2)_2OTs$	D.G.	100	300	76
$CH_3(CH_2)_5F$	$CH_3(CH_2)_5OMs$	D.G.	100	300	67
	$CH_3(CH_2)_5OBs$	D.G.	100	300	55
	$CH_3(CH_2)_5OTs$	D.G.	100	300	58

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Attempts were then made to combine the two stages—esterification and cleavage—in order to devise a continuous one-step process for conversion of hydroxyl to fluoride. For satisfactory yields in the potassium fluoride cleavage, it is advantageous to exclude all traces of sulphonyl chlorides and of ionic chloride, the latter competing with the fluoride during the cleavage. Consequently a modified preparation of sulphonates was developed in this laboratory[3](21); this involved treatment of the alcohol with a sulphonyl fluoride, in the presence of an excess of anhydrous potassium fluoride to remove the liberated hydrogen fluoride as potassium bifluoride:

$$X(CH_2)_nOH + MsF + KF \rightarrow X(CH_2)_nOMs + KFHF.$$

The cleavage of the resultant sulphonate was then effected by the excess potassium fluoride. The over-all reaction may be represented thus:

$$X(CH_2)_nOH + MsF + 2KF \rightarrow X(CH_2)_nF + MsOK + KFHF.$$

A limited number of alcohols were converted to the corresponding fluorides by this method; yields are shown in Table VII. When applied to unsubstituted alcohols this method failed at the esterification stage. From the gradation in yields obtained (Table VII: $Cl(CH_2)_2- > Cl(CH_2)_3- > Cl(CH_2)_5-$; Cl– > Br–; Cl– > MeO– > EtO–), it seems probable that a fundamental requirement is the presence in the alcohol of an electronegative group capable of exerting an inductive effect; hence the method is of very limited applicability.

TABLE VII

CONVERSION OF ALCOHOL TO FLUORIDE BY CONTINUOUS METHOD

Alcohol	Yield of fluoride, %
$Cl(CH_2)_2OH$	53[a]
	60[b]
$Cl(CH_2)_3OH$	10[a]
$Cl(CH_2)_5OH$	0[a]
$Br(CH_2)_2OH$	35[a]
$MeO(CH_2)_2OH$	43[a]
$EtO(CH_2)_2OH$	27[a]
	29[b]

[a] *Via methanesulphonate.*
[b] *Via benzenesulphonate.*

To circumvent this difficulty, a semicontinuous method was examined. Adapted from the previously reported procedure of Edgell and Parts (8), this involved the preparation of the sulphonate using the appropriate sulphonyl chloride, followed by isolation and azeotropic drying, but not purification; cleavage with potassium fluoride was then effected in the usual way. Results are summarized in Table VIII. This method affords a convenient and simple means of converting alcohols to the corresponding fluorides.

[3] *Originally developed by S. B. D. Hunt.*

TABLE VIII

CONVERSION OF ALCOHOL TO FLUORIDE BY "SEMICONTINUOUS" METHOD

Alcohol	Sulphonate intermediate	Yield of fluoride, %
$CH_3(CH_2)_5OH$	$CH_3(CH_2)_5OMs$	54
	$CH_3(CH_2)_5OBs$	54
	$CH_3(CH_2)_5OTs$	47
$CH_3(CH_2)_9OH$	$CH_3(CH_2)_9OMs$	48
	$CH_3(CH_2)_9OBs$	35

Physical constants of the fluorides prepared by the above methods are listed in Table IX.

TABLE IX

PHYSICAL CONSTANTS OF FLUORIDES

Compound	Boiling point		n_D^{25}
	°C.	mm.	
2-Fluoroethyl chloride[a]	52.5	745	1.3742
3-Fluoropropyl chloride[b]	79.5	740	1.3863
4-Fluorobutyl chloride[c]	114.5	740	1.4020
5-Fluoroamyl chloride[d]	74	76	1.4110
2-Fluoroethyl bromide[e]	73–74	750	1.4240
2-Fluoroethyl methyl ether[f]	56–57	735	1.3458
2-Fluoroethyl ethyl ether[g]	72	740	1.3582
n-Hexyl fluoride[h]	91–92	745	1.3732
n-Decyl fluoride[i]	74–75	13	1.4080
Pent-4-enyl fluoride[j]	59	735	1.3746
Ethyl fluoroacetate[k]	115–117	740	1.3750
Fluoroacetone[l]	72.5–73	740	1.3650
Ethyl 4-fluorocrotonate	53.5–54	11	1.4180

[a]*Razumovskii and Fridenberg (23) report b.p. 52–53° and* n_D^{20} *1.3775.*

[b]*Hoffmann (16) reports b.p. 82.1° and* $n_D^{27.2}$ *1.3855.*

[c]*Hoffmann (15) reports b.p. 114.7° and* n_D^{23} *1.4025.*

[d]*Hoffmann (15) reports b.p. 143.2° and* n_D^{23} *1.4120.*

[e]*Hoffmann (16) reports b.p. 71–72°.*

[f]*Schrader (25) reports b.p. 59–60° at 760 mm.*

[g]*Gryszkiewicz-Trochimowski et al. (12) report b.p. 74.5–75.5°.*

[h]*Desreux (6) reports b.p. 93.15° at 755 mm. and* n_D^{20} *1.3748.*

[i]*Swarts (28) reports b.p. 183.5°.*

[j]*Hoffmann (15) reports b.p. 61.9–62.1° at 760 mm.*

[k]*Redemann et al. (24) report b.p. 114–118° and* n_D^{21} *1.3759.*

[l]*Ray et al. (22) report b.p. 72°.*

Reactions of Chloroalkyl Sulphonates with Sodium Iodide

$$Cl(CH_2)_nOMs + NaI \rightarrow Cl(CH_2)_nI + MsONa$$

The preparations listed in Table X were studied for various reasons: (*a*) to obtain samples of the chloroiodides for other work; (*b*) to devise an improved procedure for preparing 2-chloroethyl iodide, which is inconvenient to obtain

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by other means; (*c*) to compare the procedure with the well-known half-iodination of dichloroalkanes; and (*d*) to obtain information regarding the relative reactivities of the chloride and sulphonoxy groupings in a typical S_N2 reaction.

The chloroalkyl sulphonates were allowed to react at room temperature with an equimolar quantity of sodium iodide in acetone. Yields of the corresponding chloroalkyl iodides are shown in Table X. It can be seen that the reaction is as efficient as the half-iodination procedure for which yields of 50–70% are reported (1, 13), and that 2-chloroethyl iodide can be obtained in satisfactory yield. The sulphonoxy grouping is preferentially replaced under the conditions employed.

TABLE X

PREPARATION AND PHYSICAL PROPERTIES OF CHLOROALKYL IODIDES

Compound	Yield, %	Boiling point		n_D^{25}
		°C.	mm.	
2-Chloroethyl iodide[a]	16[b]	30	12.5	
	49[c]	32–33	13	1.5615
3-Chloropropyl iodide[d]	70	58–59	13	1.5462
4-Chlorobutyl iodide[e]	59	82	10	1.5398

[a] *Meyer and Wurster (18) report b.p. 137–138°.*

[b] *From 2-chloroethyl methanesulphonate.*

[c] *From 2-chloroethyl benzenesulphonate.*

[d] *Hass and Huffman (13) report b.p. 60° at 15 mm.*

[e] *Field and Holsten (11) report b.p. 94° at 17 mm. and* n_D^{25} *1.5382.*

Reactions of Chloroalkyl Methanesulphonates with Potassium Thiocyanate

$$Cl(CH_2)_nOMs + KSCN \rightarrow Cl(CH_2)_nSCN + MsOK$$

To confirm the preferential replacement of the sulphonoxy grouping referred to above, the chloroalkyl methanesulphonates were treated with equimolar quantities of potassium thiocyanate in boiling aqueous ethanol (80%). Results and constants of the chloroalkyl thiocyanates are shown in Table XI.

TABLE XI

PREPARATION AND PHYSICAL CONSTANTS OF CHLOROALKYL THIOCYANATES

Compound	Yield, %	Boiling point		n_D^{25}
		°C.	mm.	
2-Chloroethyl thiocyanate[a,b]	69	93	14	1.5102
3-Chloropropyl thiocyanate[c]	62	115	12	1.5024
4-Chlorobutyl thiocyanate	67	134	12	1.4989
5-Chloroamyl thiocyanate	66	144–145	10	1.4950
n-Hexyl thiocyanate[d]	80	108–109	18	1.4627

[a] *Delepine and Ville (5) report b.p. 106° at 25 mm.*

[b] *Ethylene dithiocyanate,* $NCS(CH_2)_2SCN$, *was also isolated (14%), recrystallized from ethanol, m.p. 89–90°; Kaufmann and Oehring (17) report m.p. 90°.*

[c] *Henry (14) reports b.p. 222–223°.*

[d] *Cahours and Pelouze (3) report b.p. 215–220°.*

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EXPERIMENTAL[4]

TABLE XII

ANALYTICAL DATA FOR NEW COMPOUNDS

	C, %		H, %		Hal., %	
	Calc.	Found	Calc.	Found	Calc.	Found
$Cl(CH_2)_2OMs$	22.70	22.66	4.45	4.46	22.35	22.15
$Cl(CH_2)_3OMs$	27.83	27.88	5.25	5.21		
$Cl(CH_2)_4OMs$	32.18	32.12	5.94	5.75	18.99	18.95
$Cl(CH_2)_5OMs$	35.91	36.06	6.53	6.28	17.67	17.55
$Br(CH_2)_2OMs$	17.74	17.42	3.47	3.30	39.35	39.15
$CH_2{:}CH(CH_2)_3OMs$	43.90	43.69	7.32	7.43		
$MsOCH_2COOEt$	32.97	33.21	5.49	5.45		
$MsOCH_2COCH_3$	31.58	31.53	5.26	5.36		
$MsOCH_2CH{:}CHCOOEt$	40.38	40.49	5.77	5.97		
$MsOCH(COOEt)_2$	37.86	38.02	5.55	5.39		
$MsOCH_2CH(OEt)_2$	39.62	39.44	7.55	7.55		
$FCH_2CH{:}CHCOOEt$	54.54	54.44	6.82	6.66		
$Cl(CH_2)_4SCN$	40.14	40.27	5.35	5.36	23.74	23.59
$Cl(CH_2)_5SCN$	44.03	44.13	6.12	6.08	21.71	21.61

Preparation of Methanesulphonates

The following are representative examples of the procedures employed in the preparation of methanesulphonates.

Method (1). The reaction of an Alcohol with a Sulphonyl Halide

2-Chloroethyl methanesulphonate

A mixture of 2-chloroethanol (80.5 gm., 1.0 mole) and methanesulphonyl fluoride (21.7 gm., 0.22 mole) was stirred at −15°, and powdered sodium hydroxide (8.8 gm., 0.22 mole) was added in small portions. Stirring was continued at 25° for five and one-half hours. The product was diluted with water and extracted with ether. The extracts were washed with water and dried over anhydrous sodium sulphate. The ether was removed and fractionation of the residue gave 2-chloroethyl methanesulphonate (26.2 gm., 75%).

2-Chloroethyl methanesulphonate

A mixture of 2-chloroethanol (40.5 gm., 0.5 mole), methanesulphonyl fluoride (9.8 gm., 0.1 mole), and anhydrous potassium fluoride (17.4 gm., 0.3 mole) was vigorously stirred at room temperature for six hours and then allowed to stand overnight. It was diluted with water and extracted with ether. The extract was dried over anhydrous sodium sulphate, the ether removed, and the residue fractionated to give 2-chloroethyl methanesulphonate (14 gm., 88%).

3-Chloropropyl methanesulphonate

A mixture of 3-chloropropanol (71 gm., 0.75 mole) and pyridine (79 gm., 1.0 mole) was stirred in a flask cooled in an ice–salt bath, and methanesulphonyl chloride (86 gm., 0.75 mole) was added slowly over a period of one

[4]*The microanalyses were performed by Mr. J. F. Alicino, Metuchen, N.J. Results are shown in Table XII.*
Boiling points are uncorrected.
Physical constants are listed in the appropriate tables.

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and one-half hours. Stirring was continued for a further three hours. The reaction product was diluted with water and 6 *N* hydrochloric acid until there was no pyridine odor, and then extracted with ether. The extracts were washed successively with water, aqueous sodium carbonate, and water again. After drying over anhydrous calcium chloride and removal of the ether, fractionation of the residue gave 3-chloropropyl methanesulphonate (106.5 gm., 83%).

Method (2). The Reaction of a Halide with Silver Methanesulphonate

Ethyl 4-methanesulphonoxycrotonate

A mixture of ethyl 4-bromocrotonate (58 gm., 0.3 mole), silver methanesulphonate (61 gm., 0.3 mole), and acetonitrile (200 ml.) was heated under reflux on a water bath for one hour. After cooling, the precipitated silver bromide was removed by filtration and the filtrate concentrated. After a further amount of precipitate had been removed, the filtrate was taken up in ether, washed successively with water, aqueous sodium carbonate, and water again, and dried over anhydrous sodium sulphate. After removal of the ether, fractionation of the residue gave ethyl 4-methanesulphonoxycrotonate (37.3 gm., 60%).

Method (3). The Reaction of a Cyclic Ether with a Sulphonyl Halide

2-Chloroethyl methanesulphonate

Ethylene oxide (66 gm., 1.5 moles), methanesulphonyl chloride (58 gm., 0.51 mole), freshly fused zinc chloride (2 gm.), and ether (100 ml.) were placed in a stainless steel bomb, and heated at 40° for 32 hr. with constant agitation. On cooling, the solid material was removed by filtration, and the filtrate fractionated to give methanesulphonyl chloride (23.2 gm.) of b.p. 52° at 12 mm., and 2-chloroethyl methanesulphonate (27.8 gm.). This represents a yield of 50% based on reacted starting material.

2-Chloroethyl benzenesulphonate

A mixture of ethylene oxide (21 gm., 0.48 mole), benzenesulphonyl chloride (26.5 gm., 0.15 mole), and zinc chloride (0.5 gm.) was sealed in a glass ampoule and allowed to stand at room temperature (*ca.* 22°) for 70 days. The mixture was filtered to remove solid material, and the filtrate on fractionation yielded 2-chloroethyl benzenesulphonate (27 gm., 82%).

4-Chlorobutyl methanesulphonate

Tetrahydrofuran (24.6 gm., 0.33 mole), methanesulphonyl chloride (39 gm., 0.33 mole), anhydrous zinc chloride (1.0 gm.), and ether (100 ml.) were heated in a stainless steel bomb at 80° with constant agitation for four hours. On cooling, the product was filtered to remove solid material, and the filtrate fractionated to give methanesulphonyl chloride (25 gm.) of b.p. 52° at 12 mm., and 4-chlorobutyl methanesulphonate (15.7 gm.). This represents a yield of 69% based on reacted starting material.

Preparation of Fluorides

The following procedures illustrate the methods employed for the preparation of fluorides.

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2-Fluoroethyl Chloride

A mixture of 2-chloroethyl methanesulphonate (15.9 gm., 0.1 mole), potassium fluoride (11.6 gm., 0.2 mole), and methanol (200 ml.) was heated under reflux with intermittent stirring for $11\frac{1}{2}$ hr. On cooling, it was diluted with water and extracted with di-*n*-butyl ether. The extracts were dried over anhydrous sodium sulphate and on fractionation gave 2-fluoroethyl chloride (4 gm., 49%).

3-Fluoropropyl Chloride

A mixture of 3-chloropropyl methanesulphonate (17.3 gm., 0.1 mole), anhydrous potassium fluoride (11.6 gm., 0.2 mole), and diethylene glycol (200 gm.) was placed in a three-necked flask equipped with a thermometer, precision-bore stirrer, and a short still head carrying a condenser and ice-cooled receiver. The stirrer was started, the pressure in the system reduced to 320 mm., and the temperature maintained at 100°. The distillate was collected over a period of four hours, and on fractionation gave 3-fluoropropyl chloride (6.3 gm., 65%).

Ethyl 4-Fluorocrotonate

A mixture of ethyl 4-methanesulphonoxycrotonate (21 gm., 0.1 mole), anhydrous potassium fluoride (11.6 gm., 0.2 mole), and diethylene glycol (200 gm.) was placed in a flask fitted with a thermometer, precision-bore stirrer, and a still head carrying a condenser and ice-cooled receiver. The flask was heated to 100°, and the distillate was collected at a pressure of 13 mm. over a period of three hours. This was dissolved in ether, washed with water, and dried over anhydrous sodium sulphate. After removal of the ether, the residue on fractionation through a modified Podbielniak column gave ethyl 4-fluorocrotonate (6.6 gm., 50%).

2-Fluoroethyl Chloride (Continuous Method)

In the equipment described above, a mixture of 2-chloroethanol (24.1 gm., 0.3 mole), methanesulphonyl fluoride (29.4 gm., 0.3 mole), and anhydrous potassium fluoride (34.8 gm., 0.6 mole) was stirred at room temperature for 24 hr. Diethylene glycol (250 gm.) and anhydrous potassium fluoride (11.6 gm., 0.2 mole) were added, the pressure in the system was reduced to 300 mm., and the temperature raised to 100°. The distillate (16.6 gm.), collected over four hours, gave on fractionation 2-fluoroethyl chloride (13.1 gm., 53%).

n-Hexyl Fluoride (Semicontinuous Method)

n-Hexyl alcohol (15.3 gm., 0.15 mole) and pyridine (30 gm., 0.38 mole) were stirred at −15°, and to the mixture methanesulphonyl chloride (17.1 gm., 0.15 mole) was slowly added. The mixture was stirred for a further four hours and diluted with water and 6 *N* hydrochloric acid until there was no pyridine odor. The aqueous layer was extracted with methylene chloride, and the combined organic layer and extracts were washed with water. These were then transferred to the three-necked flask described above. The water – methylene chloride azeotrope was distilled, and any residual low-boiling material removed under aspirator pressure. Diethylene glycol (250 gm.) and anhydrous

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potassium fluoride (17.4 gm., 0.3 mole) were added, the temperature was raised to 100°, and the distillate collected over one and one-half hours at a pressure of 300 mm. Fractionation of this yielded *n*-hexyl fluoride (8.8 gm., 54%).

Preparation of Chloroalkyl Iodides

The preparation of 3-chloropropyl iodide is representative.

3-Chloropropyl Iodide

A mixture of 3-chloropropyl methanesulphonate (17.3 gm., 0.1 mole), sodium iodide (15.0 gm., 0.1 mole), and anhydrous acetone (100 ml.) was allowed to stand at room temperature, with occasional shaking, for 72 hr. It was diluted with water and extracted with ether. The extracts were washed successively with aqueous sodium thiosulphate and with water, and dried over anhydrous sodium sulphate. Removal of the ether and fractionation of the residue gave 3-chloropropyl iodide (10.5 gm.) and 3-chloropropyl methanesulphonate (4.5 gm.). This represents a yield of 70% based on reacted starting material.

Preparation of Chloroalkyl Thiocyanates

The preparation of 3-chloropropyl thiocyanate is representative.

3-Chloropropyl Thiocyanate

A mixture of 3-chloropropyl methanesulphonate (17.3 gm., 0.1 mole), potassium thiocyanate (9.7 gm., 0.1 mole), and 80% ethanol (25 ml.) was heated under reflux on a water bath for 16 hr. The mixture was diluted with water and extracted with ether. The extract was dried over anhydrous sodium sulphate and fractionated, yielding 3-chloropropyl thiocyanate (10 gm., 62%).

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THE ADSORPTION OF NITROGEN BY CARBON BLACK AND GRAPHITE[1]

By H. L. McDermot and B. E. Lawton

ABSTRACT

The adsorption of nitrogen by a carbon black designated as Spheron 9 has been measured at 78°K. and 71°K. The second type of hysteresis previously reported for three Acheson graphites has also been observed for the adsorption of nitrogen by Spheron 9 at both temperatures. Unlike the graphite isotherms, it was possible to scan the hysteresis loop of the Spheron isotherm. The adsorption of nitrogen has been measured for an artificial graphite in which the ash had been leached out by treatment with hydrofluoric acid. The results were compared with those obtained previously for a sample of the unleached graphite. It was found that although the surface area was altered by this treatment, the hysteresis effects remained unchanged.

INTRODUCTION

In an earlier communication (3), two hysteresis effects were reported for the adsorption of nitrogen, oxygen, and argon on three Acheson graphites at liquid nitrogen temperatures. The first of these was attributed to the porous structure of the graphite and the second to swelling of the graphite crystallites. The second type of hysteresis took the form of an initial isotherm which lay below subsequent isotherms. Except for the region of the isotherm which exhibited "pore" hysteresis, the isotherms after the first were observed to be reversible provided the sample was not fully desorbed. The upper or reversible isotherm could only be reached after a certain relative pressure had been exceeded. At relative pressures below this value, the initial isotherm was observed to be reversible, or very nearly so. By analogy with known cases of swelling hysteresis, it was postulated that this second type of hysteresis was caused by intercrystalline swelling. In the course of the work with these graphites it was found necessary for purposes of comparison to introduce an isotherm for a non-porous carbon. The adsorption isotherm of nitrogen on a non-porous carbon black (Spheron 9) was chosen. More detailed measurements on this system since publication of the earlier paper have revealed hysteresis effects similar to the second type of hysteresis observed with the graphite systems. The new work presented here includes scanning runs and an isotherm at another temperature.

In the work referred to above (3), the adsorption of gases was studied on three Acheson graphites which were used as they were received from the manufacturers. One of these graphites, which was designated by the symbol G-3, was selected for a study of the effect of ash removal. This graphite was chosen because it had a high ash content and displayed "swelling" hysteresis to the greatest extent. It will be shown that although removal of the ash displaces the isotherm downwards, it does not alter the amount of hysteresis.

EXPERIMENTAL AND RESULTS

The carbon black employed in these studies was a non-porous material

[1]*Manuscript received February 9, 1956.*
Contribution from the Defence Research Chemical Laboratories, Ottawa, Canada. Also issued as D.R.C.L. Report No. 212.

designated as Spheron 9. It was supplied to us by the Godfrey L. Cabot Co., Cambridge, Mass.

The graphite used was a sample of G-3 in which the ash content was reduced from 0.77% to 0.09% by leaching with hydrofluoric acid. This ash-free graphite will be designated as GF-3.

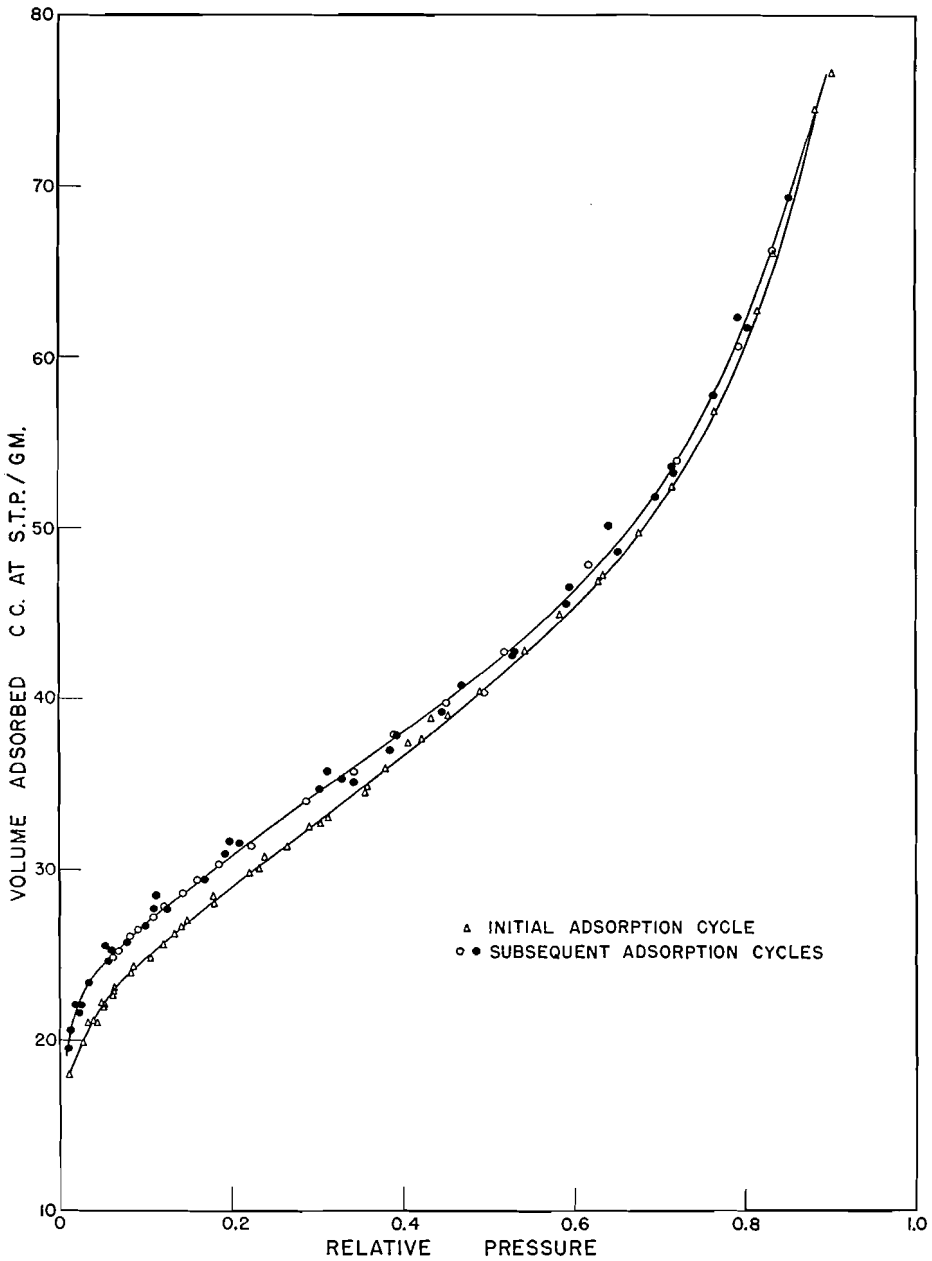

FIG. 1. Isotherm of nitrogen adsorbed by Spheron 9 at 78°K. Desorption points from the initial adsorption cycle and from subsequent cycles are represented by inked-in circles.

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Nitrogen was supplied by the Canadian Liquid Air Co. It was stated to be 99.5% nitrogen and was used without further purification.

The apparatus and procedure was exactly as described previously (3).

The adsorption isotherm of nitrogen on Spheron 9 at 78°K. is shown in Fig. 1. The triangles represent the initial adsorption curve after outgassing. The circles represent the first desorption curve as well as points taken on subsequent adsorption cycles. It will be noted that the upper curve is reversible. Scanning runs were made in which desorption was first carried out from a relative pressure of 0.356 followed by readsorption from $p/p_0 = 0.039$ to $p/p_0 = 0.514$. Desorption from this latter pressure resulted in a curve which was well within the hysteresis loop. The scanning curves along with a desorption curve from a high relative pressure are displayed in Fig. 2. In contrast

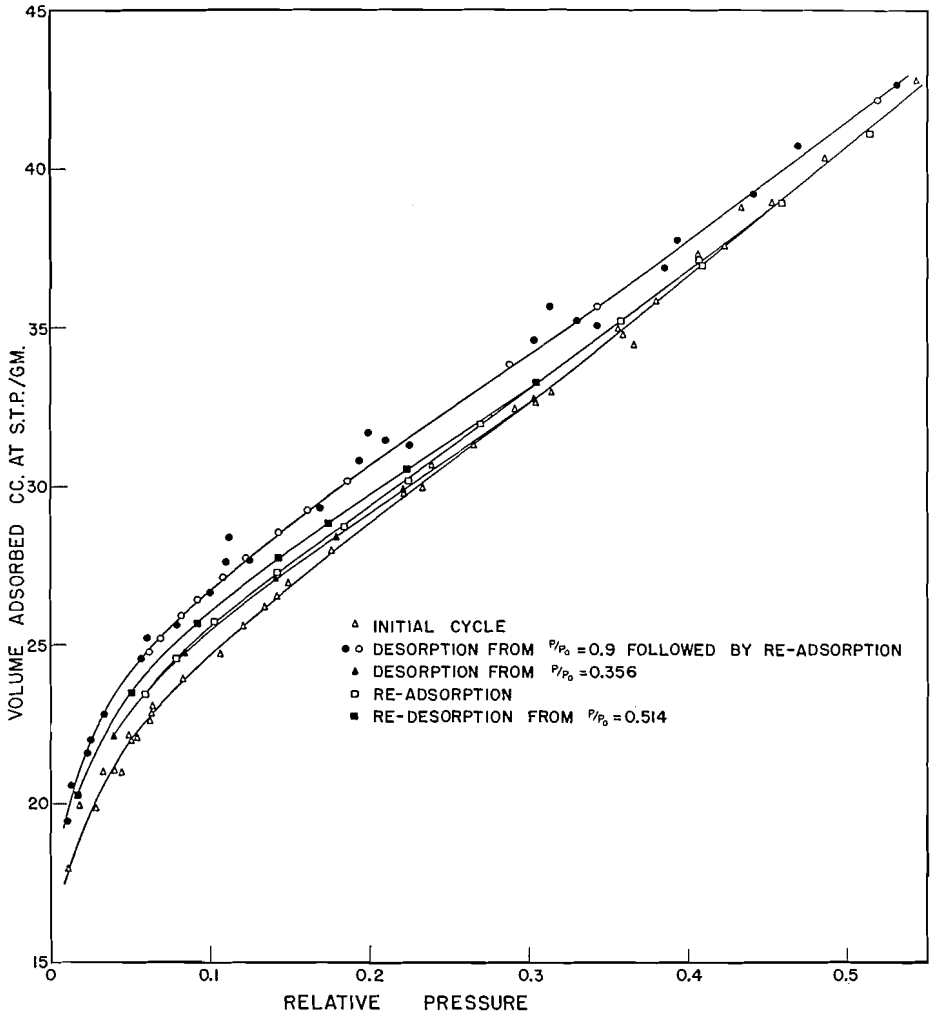

FIG. 2. Isotherm of nitrogen adsorbed by Spheron 9 at 78°K. showing the scanning runs. Desorption points are represented by inked-in symbols.

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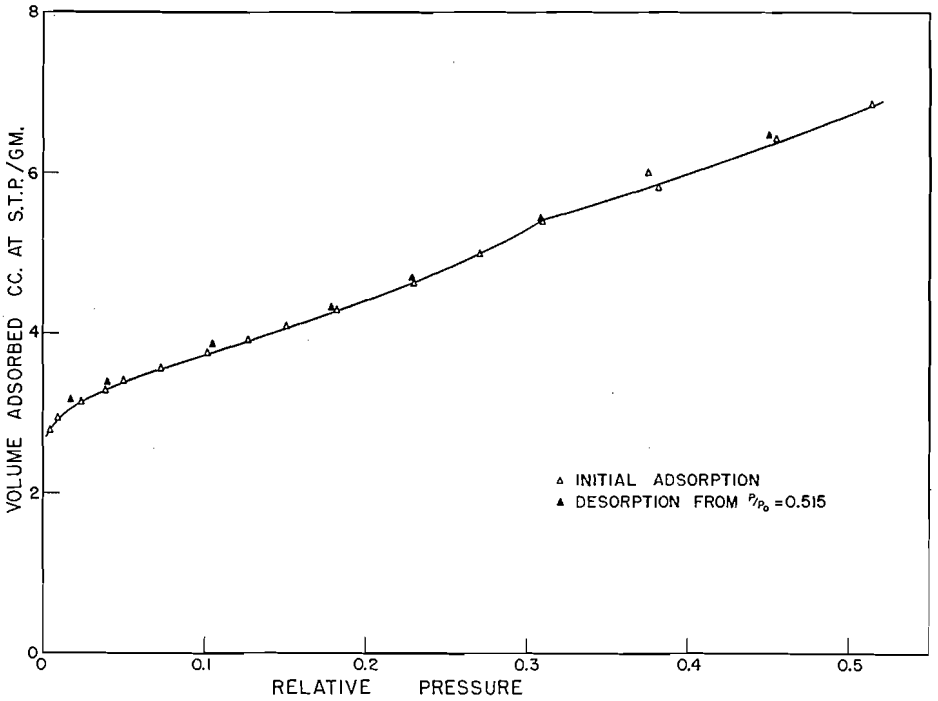

FIG. 3. Isotherm of nitrogen adsorbed by GF-3 at 71°K. illustrating desorption from moderate relative pressures. Desorption points are represented by inked-in triangles.

to the case of Spheron 9, the initial curve for graphite is very nearly reversible at moderate relative pressures. For example the isotherm shown in Fig. 3 for the adsorption of nitrogen on GF-3 at 71°K. exhibits only slight hysteresis. The adsorption of nitrogen by Spheron 9 was also measured at 71°K. The isotherm was identical in shape to the one shown in Fig. 1; therefore, it is not reproduced here. The monolayer volumes were calculated from the B.E.T. equation for the isotherms at both temperatures. They are presented in Table I along with the corresponding surface areas. The swelling process is seen to increase the surface area over its initial value by approximately 5%.

TABLE I

Temperature, °K.	Lower curve		Upper curve	
	V_m, cc. at S.T.P./gm.	S, m.²/gm.	V_m, cc. at S.T.P./gm.	S, m.²/gm.
78	23.81	104.3	25.45	111.5
71	24.96	106.1	25.89	110.0

The isotherms of nitrogen on GF-3 are presented in Figs. 3 and 4. The isotherm depicted in Fig. 3 shows that hysteresis is virtually absent when desorption occurs from moderate relative pressures (less than $p/p_0 = 0.6$). Hysteresis effects are evident in the isotherm shown in Fig. 4 when desorption

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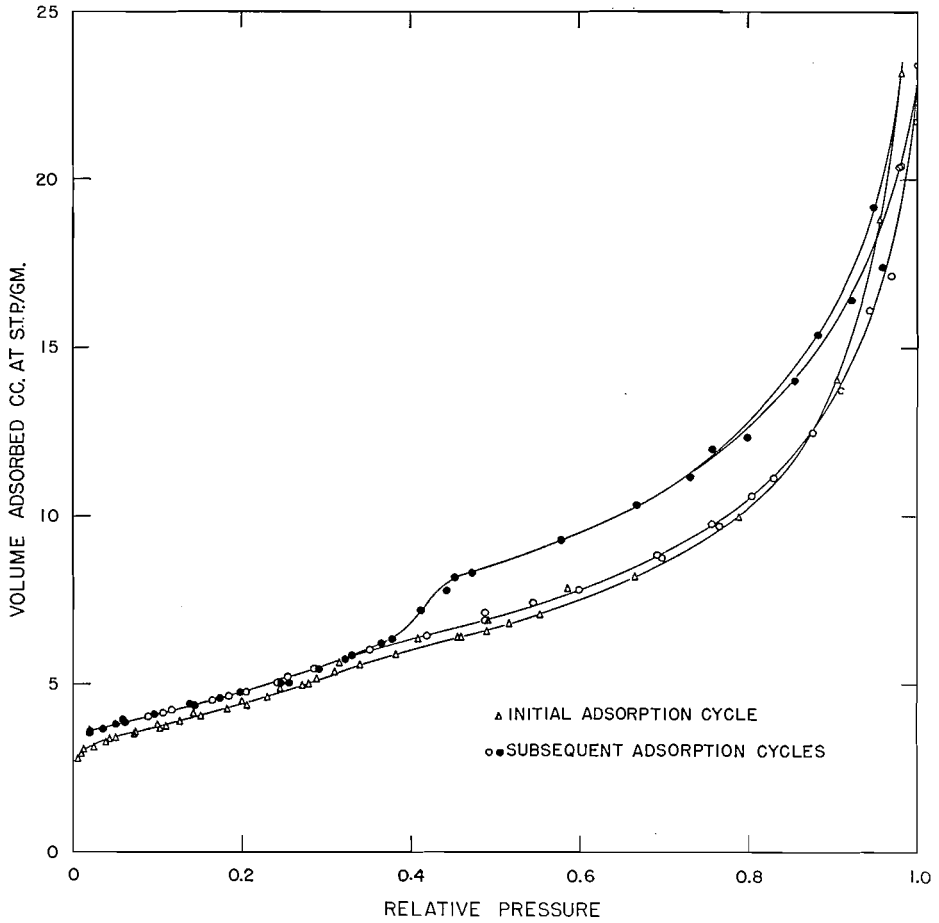

FIG. 4. Isotherm of nitrogen adsorbed by GF-3 at 71°K. Desorption points from the initial adsorption cycle and from subsequent cycles are represented by inked-in circles.

was carried out from relative pressures close to one. The quantity of nitrogen adsorbed by GF-3 is less than that adsorbed by G-3, but the hysteresis effects and the shape of the isotherm have not been changed by removal of most of the ash originally present in G-3. The monolayer volumes and corresponding surface areas for G-3 and GF-3 measured at 71°K. are compared in Table II. The difference between the volumes for upper and lower curves is the same for both graphites.

TABLE II

Graphite	Lower curve		Upper curve	
	V_m, cc. at S.T.P./gm.	S, m.²/gm.	V_m, cc. at S.T.P./gm.	S, m.²/gm.
G-3	4.44	19.0	4.73	20.1
GF-3	3.63	15.9	3.90	17.1

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DISCUSSION

It is evident from the foregoing results that Spheron 9 displays hysteresis effects similar to the second type of hysteresis shown by the Acheson graphites. This type of hysteresis has been ascribed to intercrystalline swelling (3). However, the Spheron results differ from those of graphite in one important respect. It was found possible to scan the hysteresis loop of the Spheron isotherm at moderate relative pressures. In contrast the initial adsorption curve for graphite was observed to be more or less reversible at moderate relative pressures (up to $p/p_0 = 0.5$). It was suggested in the earlier paper that the behavior of the graphite system could be explained if the swelling occurred irreversibly at a high relative pressure. Below this relative pressure the initial isotherm would be reversible or nearly so. By the same reasoning one would deduce that the Spheron swells continuously over the whole course of the isotherm. However, even in the case of Spheron the swelling does seem to become irreversible at a high enough relative pressure because the desorption curve from a high relative pressure lies on a reversible isotherm. Arnell and Barss (1) have measured the specific surface of the crystallites of Spheron 9 by X-ray diffraction methods and obtained a value of 1180 m.^{2}/gm. Comparing this value with the surface area of the particle as measured by nitrogen adsorption it can be estimated that each particle is an aggregate of about a thousand crystallites. Biscoe and Warren (2) have shown that the crystallites (or more correctly parallel layer groups) of Spheron 6 (a closely related carbon black) are composed of two-dimensional plane hexagonal nets of carbon atoms separated by essentially the same spacing as in graphite but randomly oriented about a normal to the layers. On the other hand, X-ray diffraction patterns of the Acheson graphites display the sharp lines characteristic of a regular three-dimensional graphite structure. It is logical to attribute the continuous swelling shown by Spheron to the imperfection of the crystallites. It might be expected that the adhesion would be less between the crystallites of Spheron than between those of graphite and consequently swelling occurs continuously from the very onset of adsorption. In the case of graphite a certain reduction of the surface free energy must be attained before any swelling occurs.

The work with GF-3 was undertaken to show that the hysteresis effects were not the result of inhomogeneities in the graphite structure due to the presence of inorganic matter. The isotherm in Fig. 4 demonstrates that neither the shape of the isotherm nor the amount of hysteresis is affected by the amount of ash. However, the quantity of gas adsorbed was found to be somewhat less for the ashless sample.

ACKNOWLEDGMENT

The authors wish to express their indebtedness to Dr. J. C. Arnell of the Defence Research Board for many helpful discussions and for assistance in preparing the manuscript.

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REACTION OF OXYGEN ATOMS WITH ACETALDEHYDE[1]

By R. J. Cvetanović

ABSTRACT

Reaction of oxygen atoms, produced by mercury photosensitized decomposition of nitrous oxide, with acetaldehyde has been studied at room temperature. The major products of the reaction are water and biacetyl and the only primary process appears to be

$$CH_3CHO + O \rightarrow CH_3CO + OH \quad [1]$$

followed by

$$CH_3CHO + OH \rightarrow CH_3CO + H_2O \quad [2]$$

and

$$CH_3CO + CH_3CO \rightarrow (CH_3CO)_2. \quad [3]$$

At room temperature oxygen atoms react with acetaldehyde 0.7 ± 0.1 times as fast as with ethylene, so that the activation energy of reaction [1] is likely to be close to 3 kcal./mole.

INTRODUCTION

The present work is the second in a series of investigations of the reactions of oxygen atoms with different organic compounds. In a previous publication (6) the reaction of oxygen atoms with ethylene has been described.

Oxygen atoms are produced by mercury photosensitized decomposition of nitrous oxide. It has been shown (7) that the primary step in this reaction is the formation of an atom of oxygen and a molecule of nitrogen and the rate of nitrogen production serves as a measure of oxygen atoms participating in the process. The important advantage of the use of nitrous oxide, in addition to the presence of an internal actinometer, is the absence of molecular oxygen, which by its rapid reaction with free radicals normally obscures the primary reactions of the atoms.

The reaction of oxygen atoms with acetaldehyde is of considerable interest, particularly in view of its possible participation in the process of oxidation of this compound (2, 3, 12, 13). Avramenko and Lorentso (2, 3) made an attempt to study this reaction directly, by generating oxygen atoms in O_2 and, alternatively, in H_2O. In the former case the mixture from the discharge contained O and O_2, and in the latter case it presumably contained H, O, some OH, the excess H_2O, but almost no O_2. The experiments were performed at 100° C. and the following products were observed: HCHO, CO, CO_2, organic hydroperoxides, CH_3COOH, and some HCOOH. With the H_2O discharge CH_4 and C_2H_4 were also formed. In view of the diversity of the products formed and on the basis of similar experiments with formaldehyde, these authors postulated a variety of primary steps

$$O + CH_3CHO \rightarrow CO_2 + CH_3 + H \quad [4a]$$

$$\rightarrow CHO + HCHO + H \quad [4b]$$

$$\rightarrow CH_3COOH \quad [5]$$

and came to the conclusion that $k_4 > k_5 > k_1$, i.e. that the abstraction of a

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Contribution from the Divison of Applied Chemistry, National Research Council, Ottawa, Canada. Issued as N.R.C. No. 3953.

single atom of hydrogen was the least probable of the primary processes believed to occur.

The properties ascribed to oxygen atoms by Avramenko and Lorentso are radically different from those usually assumed, notably by Geib (10) who investigated the reaction of oxygen atoms with formaldehyde. Direct experimental evidence, however, is quite scant and in the case of acetaldehyde the paper of Avramenko and Lorentso appears to be the only published work. For this reason the reaction of oxygen atoms, produced by mercury photosensitized decomposition of nitrous oxide, with acetaldehyde has been studied with the object of establishing the primary process and of obtaining some information about the rate of the reaction.

EXPERIMENTAL

The experimental arrangement has been described in detail previously (6). Acetaldehyde was a Matheson Co. product used after thorough degassing and bulb to bulb distillation *in vacuo*.

The products condensable in liquid nitrogen were fractionated on a Le Roy still (11). The "liquid products" were fractionated on a gas–liquid partition chromatographic column (5). Use has also been made of mass-spectroscopic and infrared analysis.

Quantum yields were determined relative to the rate of hydrogen production from 200 mm. of butane at 25° for which Bywater and Steacie (4) find a quantum yield of 0.50. Allowance for a slight drift in the intensity of the incident resonance radiation was made by its frequent determination and interpolation for individual runs.

RESULTS AND DISCUSSION

Relative Quenching Efficiency of Acetaldehyde

In order to establish the suitable range of experimental conditions for the study of the reaction of oxygen atoms with acetaldehyde, it was necessary first to determine the relative quenching efficiency of nitrous oxide and acetaldehyde and the products resulting from the direct mercury sensitized decomposition of the latter compound. The results of experiments with 100 mm. of nitrous oxide and varying amounts of acetaldehyde are given in Table I. Considering for the moment only the series A in Table I, it is seen that with increasing acetaldehyde the quantum yield of nitrogen (ϕ_{N_2}) decreases while the yields of the other observed products relative to R_{N_2}, i.e., to the rate of introduction of oxygen atoms into the process, increase. (With larger amounts of acetaldehyde used in this series of experiments no attempt was made to analyze for such less volatile products as water, biacetyl, or acetone.) The trend in ϕ_{N_2} is due to the competition by the two reactants for the Hg $6(^3P_1)$ atoms and the plot of $1/\phi_{N_2}$ against the acetaldehyde to nitrous oxide ratio can be used in the manner described in an earlier publication (8) to determine the relative over-all quenching efficiency of the two compounds. The plot is given in Fig. 1 and the ratio of the slope to the intercept, i.e., the

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TABLE I

MERCURY PHOTOSENSITIZED DECOMPOSITION OF MIXTURES OF 100 MM. OF NITROUS OXIDE AND VARYING AMOUNTS OF ACETALDEHYDE

Run	CH_3CHO, mm.	N_2O, mm.	ϕ_{N_2}	Relative yields of products ($R_{N_2} = 1$) CO	H_2	CH_4	C_2H_6	r.t.*	H_2O	$(CH_3CO)_2$	CH_3COCH_3	$-\Delta CH_3CHO$
Series A. Exposure 90 min., mean $I_a = 3.18\times10^{15}$ quanta sec.$^{-1}$, 23±1°C.												
36	127.6	98.9	0.202	1.50	0.321	1.05	0.223					
34	101.0	100.9	0.238	1.21	0.264	0.775	0.203					
37	68.1	100.4	0.311	0.803	0.180	0.422	0.140					
33	42.5	99.9	0.397	0.509	0.121	0.229						
35	20.5	101.3	0.539	0.254	0.040	0.074	0.019					
Series B. Exposure 120 min., mean $I_a = 2.59\times10^{15}$ quanta sec.$^{-1}$, 25±1°C.												
56	15.7	100.3	0.572	0.201	0.044	0.050		1.39	1.0	0.4	0.14	3.3
58	4.92	100.4	0.660	0.110	0.019	0.014	0.010	1.42	0.8	0.7	0.10	2.1
60	3.67	100.2	0.667	0.107	0.017	0.010		1.39				1.7
59	3.66	100.6	0.663	0.109	0.012	0.010		1.20				
57	2.52	100.5	0.728	0.141	0.018	0.011	None	1.03	0.6	0.4	0.07	1.4

*r.t. = room temperature fraction.

ratio of the over-all quenching efficiency of acetaldehyde to that of nitrous oxide, is 2.28. This value leads to the previously reported (8) relative quenching cross section of acetaldehyde.

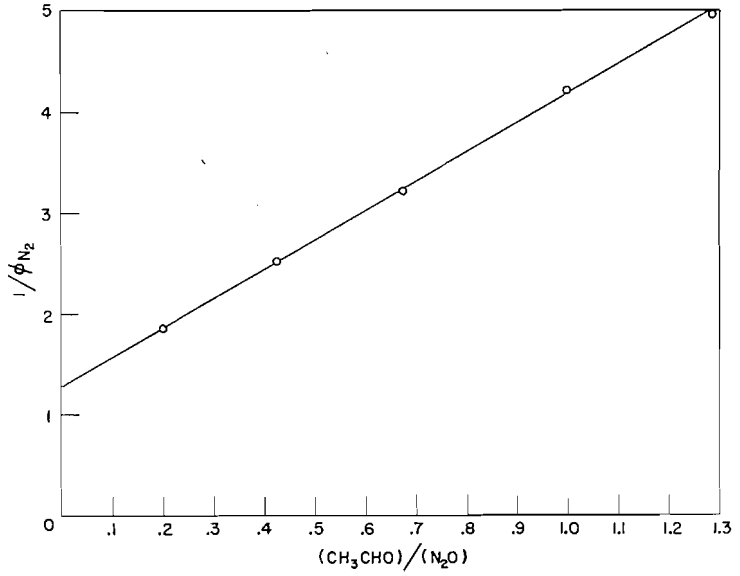

FIG. 1. Plot of the reciprocal quantum yield of nitrogen against $(CH_3CHO)/(N_2O)$ ratio. (100 mm. of N_2O, 23±1°C., mean I_a 3.18×10^{15} quanta/sec., irradiation 90 min.)

Reaction of Oxygen Atoms with Acetaldehyde

The large quenching efficiency of acetaldehyde necessitates small acetaldehyde to nitrous oxide ratios in the study of the reaction of oxygen atoms. At

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the same time at too small acetaldehyde pressures there is possibility of secondary reactions of oxygen atoms with the products formed. Fig. 2 shows

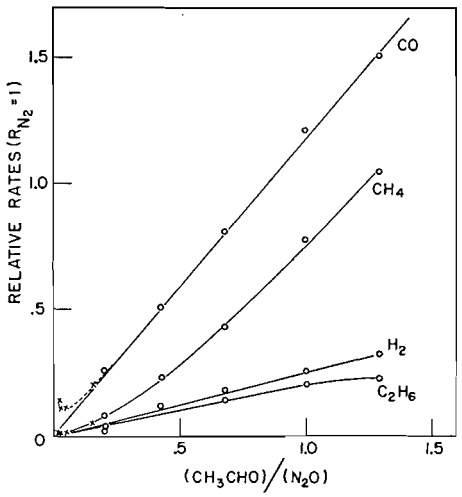

FIG. 2. Relative yields in the mercury photosensitized decomposition of 100 mm. of N_2O and varying amounts of CH_3CHO. Open circles refer to Series A and crosses to Series B, Table I.

a plot of the relative rates of formation of the more volatile products per oxygen atom introduced into the process against the CH_3CHO to N_2O ratio. For Series A the rates of formation of CO, CH_4, H_2, and C_2H_6 extrapolate to zero as the CH_3CHO to N_2O ratio approaches zero, indicating that these

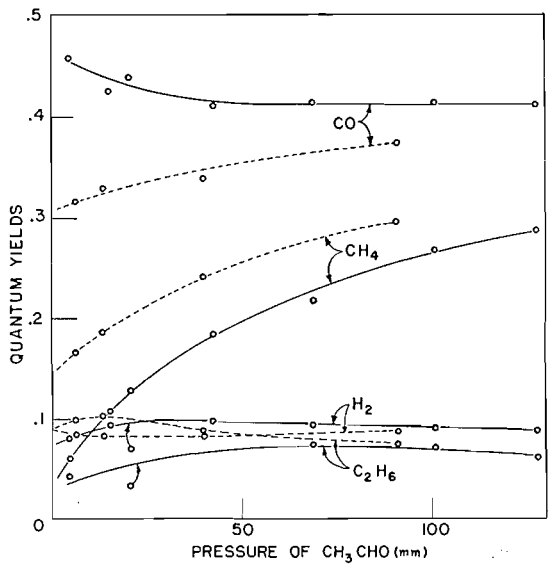

FIG. 3. Quantum yields of gaseous products in the mercury photosensitized decomposition of CH_3CHO alone (broken lines) and of its mixtures with N_2O (continuous lines) as a function of the partial pressure of CH_3CHO.

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compounds are due to quenching by acetaldehyde and not to the reaction of oxygen atoms. A few experiments with acetaldehyde alone showed that the same products were formed in the direct mercury sensitized decomposition of this compound. The results are given in Fig. 3 and it is seen that the quantum yields of these products approach at high acetaldehyde pressure those obtained from the mixtures of acetaldehyde and nitrous oxide.* The reasons for the differences at lower acetaldehyde pressures will be discussed after the primary reaction of oxygen atoms with acetaldehyde has been considered.

The results of a number of experiments with lower initial acetaldehyde pressures are given in Table I, Series B. In these experiments it was possible to isolate on the Le Roy still the acetaldehyde fraction (at $-80°$ C.) and subsequently the residual "room temperature" fraction. Both these fractions were analyzed by gas–liquid partition chromatography and by mass-spectrometric methods. The former was found to contain in addition to the unreacted acetaldehyde appreciable amounts of acetone, and the latter large amounts of biacetyl and water. These compounds were not found in the mercury sensitized decomposition of acetaldehyde alone. No other compounds were detected and, in particular, mass spectrometer analysis of the "room temperature" fraction showed absence of acetic acid and alcohols.

The formation of biacetyl and water as the major products under the conditions of the series B of experiments indicates that the following reactions occur:

$$CH_3CHO + O \rightarrow CH_3CO + OH, \quad [1]$$

$$CH_3CHO + OH \rightarrow CH_3CO + H_2O, \quad [2]$$

$$CH_3CO + CH_3CO \rightarrow (CH_3CO)_2. \quad [3]$$

In the absence of any other reactions, the relative rates per oxygen atom would be for water and biacetyl unity and for the consumption of acetaldehyde two. Several other reactions involving CH_3CO radicals must, however, be also considered. Since a certain amount of direct quenching by acetaldehyde occurs even in the experiments where quite small quantities of this compound are used, methyl radicals are also present and their combination with CH_3CO explains the formation of some acetone. Ausloos and Steacie (1) have suggested also abstraction of hydrogen from CH_3CO by CH_3 radicals and disproportionation of two CH_3CO radicals to form ketene and acetaldehyde. In view of this, the relative yield of biacetyl will be lower than unity as a result of the reactions

$$CH_3CO + CH_3 \rightarrow CH_3COCH_3, \quad [6]$$

$$CH_3CO + CH_3 \rightarrow CH_4 + CH_2CO, \quad [7]$$

$$CH_3CO + CH_3CO \rightarrow CH_3CHO + CH_2CO, \quad [8]$$

and possibly to a small extent also

$$CH_3CO \rightarrow CH_3 + CO. \quad [9]$$

At very small acetaldehyde pressures, on the other hand, there is also the possibility of incomplete utilization of O-atoms in reaction [1] and of OH

**The latter quantum yields were calculated relative to the fraction of the incident radiation quenched by acetaldehyde.*

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radicals in reaction [2] because of their reactions with the compounds or free radicals formed.* As the acetaldehyde pressure becomes larger the relative yield of biacetyl would be expected to increase and, after reaching a maximum value smaller than unity, to start to decrease again because of the increasing importance of reactions [6] and [7]. The trends in the yields of biacetyl, water, and acetone, and in the consumption of acetaldehyde in the series B of experiments, Table I, are in agreement with these interpretations, although lack of knowledge of the rate constants of the reactions involved and the considerable difficulty of accurately analyzing for these products preclude a detailed quantitative treatment. With the huge amounts of nitrous oxide used no attempt was made to analyze for ketene.

The deviations in Fig. 3 at lower acetaldehyde pressures of the quantum yields of the products resulting from direct quenching by acetaldehyde alone and in the presence of nitrous oxide are understandable in view of the occurrence of reactions [6] to [9]. Methyl radicals are undoubtedly a primary product of the mercury sensitized decomposition of acetaldehyde. Acetyl radicals, on the other hand, appear to be produced in the studied process only by the action of oxygen atoms and then, as a result of reactions [6] and [7], lead to a decrease in CH_3 radical concentration and, therefore, also to a smaller production of methane and ethane (by abstraction and recombination, respectively). The somewhat increased formation of carbon monoxide in the presence of oxygen atoms may be due to some occurrence of reaction [9] and to secondary processes. An evidence for the latter is found in the results given in Table II for a series of experiments with 100 mm. N_2O and 3.6 mm. CH_3CHO

TABLE II

THE EFFECT OF REACTION TIME ON THE RELATIVE YIELDS OF GASEOUS PRODUCT PER OXYGEN ATOM CONSUMED

(Mean I_a 1.76×10^{15} quanta/sec., 100 mm. N_2O and 3.6 mm. CH_3CHO)

Run	Temp., °C.	Irradn., min.	ϕ_{N_2}	Relative yields (R_{N_2} = 1)		
				CO	H_2	CH_4
24	25.3	60	0.64	0.109	0.014	0.011
25	26.2	120	0.65	0.111	0.006	0.017
18	26.9	180	0.64	0.121	0.013	0.007
26	25.7	240	0.66	0.130	0.016	0.009
23	25.1	300	0.65	0.147	0.021	0.009

irradiated for different lengths of time. There is a distinct increase in the relative yield of carbon monoxide with increasing reaction time. The extrapolated initial yields, after allowing for the direct quenching by acetaldehyde, are quite small.

**Various reactions of this type could be suggested, for example those of O-atoms or OH radicals between themselves or with acetyl radicals, leading perhaps in the latter case to the formation of acetic acid. No acetic acid, however, is detected in the product. Although it could be argued that this compound might undergo further attacks once it is formed, postulates of this kind would be very speculative in the absence of any supporting evidence. At present it would seem better not to attempt to specify these processes in any detail. Their net effect, as well as of possible analogous reactions involving the products, must be a decrease in the yields of biacetyl and water at very small acetaldehyde pressures.*

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The present experiments indicate that the only mode of reaction of oxygen atoms with acetaldehyde is the abstraction of the aldehydic hydrogen atom to give an OH and a CH_3CO radical. This result is in disagreement with the postulates of Avramenko and Lorentso (2, 3), who consider the abstraction of the hydrogen atom to be the least probable of the assumed several distinct modes of primary reaction. It ought to be pointed out, however, that the experiments of these authors were conducted at a higher temperature where CH_3CO radicals are known to decompose readily. A further complicating feature might have been the presence of relatively large concentrations of hydrogen atoms and possibly also of some molecular oxygen even in the H_2O discharge.

Estimate of the Activation Energy of the Reaction

In order to obtain information on the rate of the reaction of oxygen atoms with acetaldehyde, several experiments were conducted at 25° C. with mixtures of 300 mm. of N_2O and varying ratios of smaller amounts of CH_3CHO and C_2H_4. To minimize any depletions of the reactants in the course of the reaction a circulating system of total volume 500 ml. was employed. The results are given in Table III. Direct quenching by C_2H_4 resulted, at the high total

TABLE III

EXPERIMENTS WITH MIXTURES OF 300 MM. OF N_2O AND VARYING AMOUNTS OF CH_3CHO AND C_2H_4 (25±1°C., CIRCULATING SYSTEM)

Run	CH_3CHO, mm.	C_2H_4, mm.	$\frac{CH_3CHO}{C_2H_4}$	Irradn., min.	R_{N_2}, molec.cc.$^{-3}$ sec.$^{-1}$ $\times 10^{-15}$	Relative rates (R_{N_2} = 1)			
						CO	CH_4	H_2	$-\Delta C_2H_4$
73	—	51.3	—	65	1.23	0.471	0.146	0.078	
72	4.83	51.6	0.094	60	1.21	0.448	0.143	0.095	
71	5.15	19.9	0.259	60	1.42	0.404	0.125	0.072	
70	4.90	9.94	0.493	60	1.49	0.378	0.117	0.064	0.917
69	4.73	4.94	0.961	60	1.51	0.332	0.106	0.068	
76	2.44	1.06	2.30	60	1.69	0.251	0.048	0.059	0.484
78	4.90	1.06	4.64	60	1.63	0.244	0.040	0.043	0.280
79	7.92	1.06	7.49	60	1.71	0.185	0.036	0.040	
81	8.03	1.06	7.61	120	1.79	0.189	0.035	0.041	0.190
75	4.74	0.524	9.05	60	1.64	0.179	0.030	0.043	
74	4.82	—	∞	60	1.63	0.126	0.010	0.002	—

NOTE: *the R_{N_2} values are not strictly comparable between themselves since the reaction cell was occasionally flamed and the transparency of the front window fluctuated to some extent. Mean I_a remained about 2.3×10^{15} quanta/sec.*

pressures used, in essentially complete collisional deactivation. The processes to be considered in addition to reactions [1] and [2] are

$$C_2H_4 + O \rightarrow \text{Products} \qquad [10]$$

and

$$C_2H_4 + OH \rightarrow \text{Products.} \qquad [11]$$

The products of reaction [10] are known (6, 9), while no information on reaction [11] appears to be available. It will be assumed, subject to subsequent justification, that reaction [11] cannot compete successfully with reaction [2]

for OH radicals under the conditions of the experiments performed. It is then possible to evaluate k_1/k_{10} by comparing the relative rates of formation of different products or of the consumption of the reactants as CH_3CHO to C_2H_4 ratio is varied, since it was found that this ratio remained virtually unaltered in the course of reaction with the amounts and conversion levels used. Thus, in the reaction of oxygen atoms with about 1 mm. ethylene in the presence of 300 mm. N_2O the relative rate of over-all consumption of ethylene per oxygen atom is about 1.2. If in the mixtures of C_2H_4 and CH_3CHO the latter compound does not interfere with the reaction of O-atoms with ethylene except by using some of the available O-atoms, the following relationship would be expected to hold

$$\frac{R_{N_2}}{R_{C_2H_4}} = 1.2\left(1 + \frac{k_1}{k_{10}}\frac{(CH_3CHO)}{(C_2H_4)}\right).$$

The plot of $R_{N_2}/R_{C_2H_4}$ vs. $(CH_3CHO)/(C_2H_4)$ is given in Fig. 4 and the value of k_1/k_{10} obtained from the slope to intercept ratio is 0.68. In a similar manner,

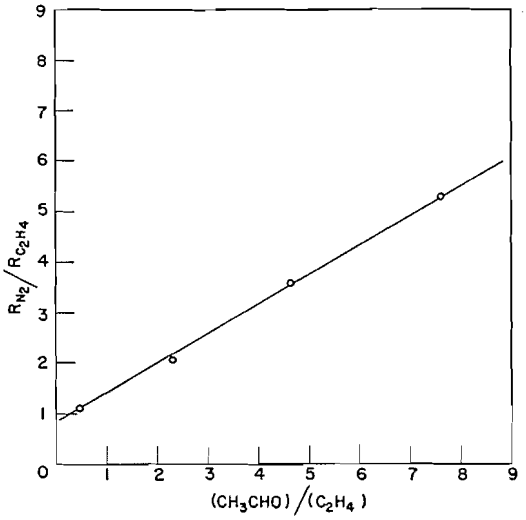

FIG. 4. Plot of the reciprocal rate of C_2H_4 consumption per oxygen atom vs. $(CH_3CHO)/(C_2H_4)$ ratio.

if any one of the relative rates per oxygen atom ($\zeta = R/R_{N_2}$) has a value α with C_2H_4 alone and β with CH_3CHO alone, then

$$\epsilon = \frac{\zeta-\alpha}{\beta-\zeta} = \frac{k_1}{k_{10}}\frac{(CH_3CHO)}{(C_2H_4)}.$$

In Fig. 5 are given the plots of ϵ against $(CH_3CHO)/(C_2H_4)$ for CO and CH_4 with the respective α and β values as found experimentally in runs 73 and 74 (Table III). There is a considerable scatter of points, which is readily explainable by limitations in analytical accuracy. A corresponding plot for the relatively small H_2 production is for the same reason much too uncertain, although the

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trend is qualitatively the same. The results for CO and CH_4 are mutually in reasonably good agreement and the slope of what appears to be the best line through the points gives 0.64 as the value of k_1/k_{10}.

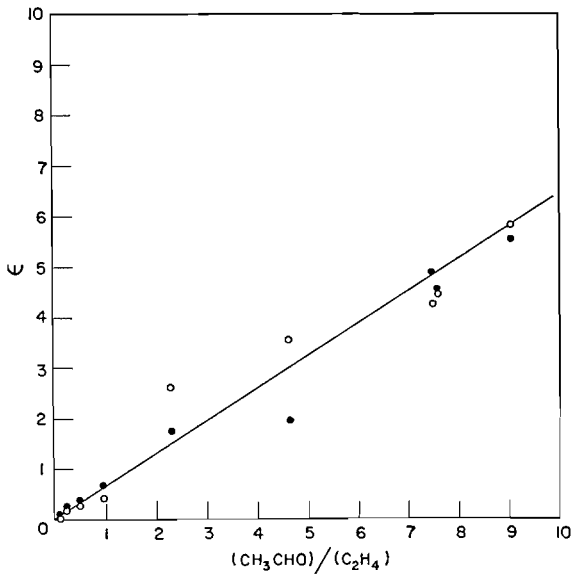

FIG. 5. Plots of ϵ_{CH_4} (open circles) and ϵ_{CO} (filled circles) vs. $(CH_3CHO)/(C_2H_4)$ ratio.

The value of k_1/k_{10} can also be estimated by comparing the rates of consumption of the two reactants. If the over-all consumption of C_2H_4 per oxygen atom is about 1.2 and that of CH_3CHO is presumably 2, the following relationship would be expected to hold

$$\frac{k_1}{k_{10}} = \frac{1.2}{2}\,\frac{(C_2H_4)}{(CH_3CHO)}\,\frac{R_{CH_3CHO}}{R_{C_2H_4}}.$$

It is difficult to determine accurately the rate of CH_3CHO consumption, in particular since some aldehydes are a product of the reaction of O-atoms with C_2H_4 (6). However, by applying reasonable corrections the values of R_{CH_3CHO} in addition to the corresponding $R_{C_2H_4}$ were obtained for two runs. In both cases k_1/k_{10} was thus found to be somewhat larger than 0.6 with probable uncertainty not greater than about 20%.

The values of k_1/k_{10} obtained in different ways are therefore mutually consistent and it appears reasonably certain that at room temperature $k_1/k_{10} = 0.7 \pm 0.1$. In view of this it is likely that E_1 is close to 3 kcal./mole, the value recently estimated (6) for reaction [10]. The work now in progress with a number of olefinic hydrocarbons with the use of improved analytical techniques (5) may provide means for additional verification of these values and for eventual determination of the activation energy differences for a number of reactions of oxygen atoms with common organic compounds.

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The consistency of the k_1/k_{10} values obtained in different ways provides justification for the earlier made assumption that OH radicals react preferentially with acetaldehyde. The alternative assumption that in the performed experiments oxygen atoms reacted exclusively with CH_3CHO and that the observed trends were due to a competition for OH radicals rather than for O-atoms is highly unlikely. This assumption would require that OH radicals form with ethylene the same type of products and moreover in the same ratio as are formed in the interaction of oxygen atoms with ethylene. The results in Table III show that the yields of CO, CH_4, and H_2 approach those obtained with C_2H_4 alone as the $(CH_3CHO)/(C_2H_4)$ ratio approaches zero and in the reaction of O-atoms with C_2H_4 no OH radicals are formed.

ACKNOWLEDGMENT

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THE COMPOSITION OF THE STRONG PHOSPHORIC ACIDS[1]

By Anna-Liisa Huhti and Phoebus A. Gartaganis

ABSTRACT

The composition of the strong phosphoric acids was studied in the range 68.8 to 86.3% phosphorus pentoxide by weight. Improved filter-paper chromatography made possible the quantitative determination of the nine lower members of the series, and occasionally up to the twelfth member. It was found that when the strong phosphoric acids are prepared by heating at 350°C., a dynamic equilibrium between the component acids is set up which persists when the mixtures are cooled to room temperature. Only linear condensed polyphosphoric acids were present in the range studied. The composition corresponding to 100% orthophosphoric acid contains about 6 mole per cent each of pyrophosphoric acid and "free water". As the mole ratio of water to phosphorus pentoxide decreases, the number of component acids increases. Orthophosphoric acid is present to an appreciable extent in the stronger phosphoric acids. "Hexametaphosphoric acid" is not a separate chemical entity, but a mixture of higher linear polyphosphoric acids.

INTRODUCTION

The composition of the strong phosphoric acids,* i.e. acids containing more than 72.4% by weight of phosphorus pentoxide, the P_2O_5 content of pure orthophosphoric acid, is a subject of considerable interest which has been repeatedly investigated by wet analytical methods. Difficulties in these methods, however, have set a decided limitation on the qualitative and quantitative conclusions possible. A study of this subject by filter-paper chromatography was undertaken, therefore, in order to obtain further and more specific information about compositions having a mole ratio of water to phosphorus pentoxide between 3.6 and 1.2.

It has been shown by means of paper chromatography that by mixing orthophosphoric acid with phosphorus pentoxide at different ratios, and heating the mixture at 350°C., we obtain a mixture containing only linear condensed polyphosphoric acids. No cyclic ones were found. Branched acids, if present, would not be detected, since any ion-molecules with branching are expected to hydrolyze immediately upon dissolution (40). A certain characteristic equilibrium mixture exists for every given ratio of water to phosphorus pentoxide.

The phosphoric acids are very viscous, so that equilibria are attained very slowly; the end result of cooling is an oil in the range 72 to 82% P_2O_5, a gum in the range 82 to 86% P_2O_5, and a brittle glass at higher P_2O_5 concentrations. These acids are merely members of a continuous series of amorphous condensed phosphoric acid mixtures which extends from orthophosphoric acid to pure phosphorus pentoxide (38). These mixtures are hygroscopic and hydrolyze upon standing unless stored in tightly closed pyrex containers.

The existence of strong phosphoric acids has been known for many years. Durgin, Lum, and Malowan (14) give a list of several such acids reported

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previously in the literature. Some of these have since then been positively identified, e.g. the tetrapolyphosphoric acid, $H_6P_4O_{13}$, while for others there is enough evidence to date to make their existence highly improbable, e.g. the metaphosphoric acid monomer, HPO_3. Finally, some of the acids listed by the above-mentioned authors, which at the time represented merely theoretical combinations of phosphorus pentoxide and water, have during the present study been positively identified as far as this is possible by paper chromatography, and their relative concentrations in several mixtures accurately established, e.g. "hexerohexaphosphoric" acid, $H_8P_6O_{19}$, better known today as hexapolyphosphoric acid. The same authors checked the analytical methods of Gerber and Miles (19) against those of Britske and Dragunov (6) and found an increasing divergence when acids of high phosphorus pentoxide content were being analyzed. This they considered as evidence that polyphosphoric acids may be present in the strong phosphoric acids.

Bell (3) went a step further by recognizing that tripolyphosphoric acid is present and interferes in some procedures for pyrophosphate determination. By using an analytical method previously developed by the same author (5), he was able to show the presence of ortho-, pyro-, and tripolyphosphoric acids in several of the strong phosphoric acid mixtures, and of "the polymer of metaphosphoric acid commonly known as hexametaphosphoric acid". An "unidentified" acid, indicated by difference, was also present between 78 and 88% phosphorus pentoxide.

Although the exact composition of the strong phosphoric acid mixtures had not been established, several of their physical and chemical properties as a function of their phosphorus pentoxide content were reported in the literature. These include, among others, measurements of densities (14, 23), viscosities (14), vapor pressures (7), boiling points and composition of the vapor over the boiling mixture (38), and heats of vaporization (38). By boiling orthophosphoric acid an azeotropic mixture was obtained (b.p. 869°C., 753 mm. Hg) containing 92.1% phosphorus pentoxide (34). Vapor-density measurements indicated that the vaporized acids dissociate into water and phosphorus pentoxide at temperatures near 1000°C. (38).

EXPERIMENTAL AND RESULTS

Analytical Methods

Various methods exist for the analysis of phosphate mixtures. Considerable effort has been spent during the last 50 years on developing traditional wet-chemical methods (2, 3, 6, 15, 19, 25, 33) for determining the various species of phosphates in the presence of one another. These methods were not adequate since they could not separate the acids higher than tripolyphosphoric acid. These higher acids are present in many strong phosphoric acid mixtures and interfere with the analysis. None of the methods has proved very satisfactory. This has recently been clearly demonstrated for mixtures of pyro- and tripolyphosphate by Dewald (13). The most commonly used wet-chemical methods are those of Jones (24) and Bell (5). Both these procedures are satisfactory for routine determinations on a given industrial product, although the absolute values may be considerably in error. According to the

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Bell procedure, no distinction is possible between polyphosphates with more than four phosphorus atoms in their chain. The zinc precipitation method of Raistrick, Harris, and Lowe (28) does not tolerate large amounts of orthophosphate, while the various X-ray methods, such as the one developed by Raistrick (27), are of course limited to crystalline mixtures. The temperature rise method of McGilvery (26) has so far only found application to sodium tripolyphosphate mixtures containing Phases I and II. The infrared technique of Corbridge and Lowe (10) is sensitive to differences of crystalline form but quantitative methods for amorphous phosphates have not been reported. The sensitivity of the end-group titration methods of Samuelson and Van Wazer (32, 40) decreases with increasing chain length.

As compared with these methods, the paper chromatographic procedure combined with differential spectroscopy (18) permits the direct determination of more species of phosphate anions with as good or better accuracy.

Chromatographic Analysis

The analyses were made using a procedure developed in this laboratory and described in previous papers (11, 42). This method involves the separation of the phosphate components by filter-paper chromatography and the subsequent colorimetric determination of the phosphorus content of each component. The precision of the method is an absolute figure varying from ± 0.5 to $\pm 1.0\%$ of the total phosphorus present, depending on the number and species of phosphates present.

The following modifications of the above-mentioned method have been introduced. In addition to the rectangular chromatographic tanks already in use, cylindrical containers (height 43 cm., diameter 24 cm.) were employed to perform bidimensional base–acid analyses as described by Ebel and his coworkers (16). This method makes possible the clear separation and differentiation of condensed cyclic and linear polyphosphates. The phosphate solution was spotted at the base of a cylindrically shaped 58×22 cm. Schleicher and Schuell No. 589 Green Ribbon filter paper, placed inside the cylindrical tank. This was filled 1 cm. deep with the basic solvent (17) consisting of

40 cc. isopropanol,
20 cc. isobutanol,
39 cc. water,
1 cc. ammonia (25%).

After 24 hr. the paper was dried and placed in a tank containing the acid solvent (31) consisting of

70 cc. isopropanol,
20 cc. trichloracetic acid (25%),
10 cc. water,
0.3 cc. ammonia (25%).

This solvent is very similar to those described by Volmar, Ebel, and Yacoub (16), and Grunze and Thilo (22). The direction of movement of the solvent in the two cases were perpendicular to each other.

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The method of Consden, Gordon, and Martin (9), which uses filter-paper chromatograms with downward solvent flow, has been abandoned in favor of ascending chromatographic techniques. The resulting slowing down of the movement of the solvent produced a better separation of phosphates with chains from 5 to 11 phosphorus atoms. The paper was cut in strips approximately 30×13 cm., with the lower end pointed and ending in a narrow projection, 1 cm. wide, dipping into a beaker filled with fresh solvent.

The running time varied from 16 to 24 hr., the temperature being kept constant at 17°C. No correction was made for any hydrolysis occurring during the running of the chromatogram. Hydrolysis studies since show that the principal effect of hydrolysis would be to reduce the values for hypoly- and raise that for pyro- and to a lesser extent ortho-. Intermediate chain lengths would probably gain as much as they would lose. The hydrolysis error was estimated not to exceed one per cent of the total phosphorus in the values given in Table III except in the cases where hypoly- is a major constituent, in which case the hypoly- may be underestimated by as much as 20% of its true value, the other components being uniformly overestimated accordingly. It has not been possible to compare against standard solutions in the case of acids with more than four phosphorus atoms, since they have so far not been isolated.

Materials

Orthophosphoric acid, 85%, 0.0001% As, Merck (87.1% H_3PO_4 by analysis).

Phosphorus pentoxide, min. 98%, 0.005% As, Merck (98.0% P_2O_5 by analysis).

Sodium phosphate monobasic monohydrate, Merck, $NaH_2PO_4.H_2O$.

Sodium phosphate dibasic anhydrous, Merck, Na_2HPO_4.

Sodium pyrophosphate decahydrate, Merck, $Na_4P_2O_7.10H_2O$.

Sodium tripolyphosphate anhydrous, techn. ERCO. Purified by successive recrystallizations from an ethanol–water mixture.

Sodium tetrapolyphosphate. Sodium tetrametaphosphate was hydrolyzed in a 5 *N* sodium hydroxide solution, and precipitated as an oil with ethanol.

Sodium trimetaphosphate. $NaH_2PO_4.H_2O$ was heated four hours at 1100°C. and then 24 hr. at 550°C. It was recrystallized from aqueous solution with ethanol.

Sodium tetrametaphosphate (Cyclophos), Victor Chemical Works. Purified by successive recrystallizations from an ethanol–water mixture.

Preparation of the Acids

A series of mixtures having a mole ratio of H_2O to P_2O_5 between 3.6 and 1.2, i.e. a phosphorus pentoxide content between 68.8 and 86.3% by weight, were prepared by placing 15 to 25 gm. phosphoric acid and phosphorus pentoxide in a 50-ml. Erlenmeyer flask, flame sealing, and heating it in a furnace at approximately 350°C. for about 10 to 20 min. Vigorous shaking in the furnace helped to obtain a uniform mixing of the materials. The heating was interrupted before or immediately after the acids started to attack the Pyrex container. After the mixture had cooled to room temperature, the flask was broken open; a sample was withdrawn and neutralized with 1 *N* sodium

hydroxide to the phenolphthalein end point. All the strong phosphoric acids hydrolyze when dissolved in water and revert finally to orthophosphoric acid. The rate of hydrolysis (12, 21, 39) is very dependent on temperature and the pH of the solution; at room temperature and at a pH 8 to 10 the rate is extremely slow. In order to prevent hydrolysis, care was taken to dilute the acid mixture as quickly as possible, while keeping the pH near the phenolphthalein end point and cooling the sample in crushed ice. A small drop of this solution was analyzed by means of paper chromatography.

For several samples, the phosphorus pentoxide content, calculated from the weight of the starting materials, was found to be in agreement with the total P_2O_5 determined by direct pH titration (1) after complete hydrolysis.

Preliminary experiments were used to assess the importance of the experimental conditions.

(*a*) It was soon established that the relative proportion of the component phosphoric acids is a function of the over-all concentration of phosphorus pentoxide only and does not depend on the method of preparation. Mixtures were prepared by evaporating orthophosphoric acid in pyrex containers, in a graphite crucible, and in a platinum crucible respectively. In each case the composition of the mixture obtained corresponded to that found when the acids were prepared in sealed Erlenmeyer flasks. Durgin *et al.* (14) and Bell (3) arrived earlier at the same conclusion.

(*b*) As shown in Table I, the time of heating had no significant effect on the analysis of the solutions obtained, provided a clear melt was obtained before the glass was attacked.

TABLE I

EFFECT OF TIME OF HEATING ON COMPOSITION OF STRONG PHOSPHORIC ACID MIXTURES
(P_2O_5 content: 77.6%; temperature: 300°C.)

Time (min.)	Distribution of total phosphorus (wt. %)				
	Ortho-	Pyro-	Tri-	Tetra-	Penta-
3	30.9	48.5	14.8	4.3	1.5
5	31.0	48.3	15.7	3.9	1.1
10	32.9	48.1	14.4	3.8	0.8
30	32.6	47.6	14.3	4.5	1.0

TABLE II

EFFECT OF TEMPERATURE OF PREPARATION ON COMPOSITION OF STRONG PHOSPHORIC ACID MIXTURES
(P_2O_5 content: 77.6%; heating time: 5 min.)

Temp. (°C.)	Distribution of total phosphorus (wt. %)				
	Ortho-	Pyro-	Tri-	Tetra-	Penta-
250	30.6	49.3	14.5	4.8	0.8
300	32.0	47.9	14.3	4.6	1.2
344	30.9	48.2	14.8	4.8	1.3
405	30.8	48.8	14.7	4.8	0.9

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(*c*) The effect of the temperature of preparation on the composition of the mixture is shown in Table II. It will be noted that the temperature range covered was not very large, but was sufficient to show that the temperature of preparation was not a critical factor in these experiments.

The principal experiments were concerned with mixtures having a phosphorus pentoxide content ranging from 68.8 to 86.3%. The results are presented in Table III and plotted in Figs. 2 and 3. In the latter the vertical distance between the curves represents the concentration of the phosphoric acid indicated by number, expressed in per cent P_2O_5 by weight.

TABLE III

COMPOSITION OF STRONG PHOSPHORIC ACIDS

Composition (wt. % P_2O_5)	Per cent of total phosphorus as:									
	Ortho-	Pyro-	Tri-	Tetra-	Penta-	Hexa-	Hepta-	Octa-	Nona-	"Hypoly-"
68.80	100.00	Trace								
69.81	97.85	2.15								
70.62	95.22	4.78								
72.04	89.91	10.09								
72.44	87.28	12.72								
73.43	76.69	23.31								
74.26	67.78	29.54	2.67							
75.14	55.81	38.88	5.31							
75.97	48.93	41.76	8.23	1.08						
77.12	39.86	46.70	11.16	2.28						
78.02	26.91	49.30	16.85	5.33	1.60					
78.52	24.43	48.29	18.27	6.75	2.26					
79.45	16.73	43.29	22.09	10.69	4.48	1.92	0.80			
80.51	13.46	35.00	24.98	13.99	6.58	3.14	2.84			
81.60	8.06	27.01	22.28	16.99	11.00	5.78	3.72	2.31	1.55	1.28
82.57	5.10	19.91	16.43	16.01	12.64	8.89	6.41	4.11	3.51	6.99
83.48	4.95	16.94	15.82	15.91	12.46	9.71	6.77	5.04	2.99	9.42
84.20	3.63	10.60	11.63	13.05	12.17	9.75	8.19	5.92	4.91	20.16
84.95	2.32	6.97	7.74	11.00	10.45	9.62	8.62	7.85	6.03	29.41
86.26	1.54	2.97	3.31	5.16	5.32	5.54	3.51	3.30	3.30	66.03

N.B. The figures are given to two decimal places for further computation purposes, but the precision may not be better than one per cent total phosphorus in some cases.

DISCUSSION

Both our work and that of earlier authors support the view that, when the strong acids are prepared by heating, a dynamic equilibrium between the component acids is set up which is metastably frozen in when the mixtures are cooled to room temperature. Methods used to date to study these mixtures have been largely based on analytical or crystallization techniques.

Analysis

Our analyses based on paper chromatography agree roughly with those of Bell (3) based on wet-chemical methods as far as the low molecular weight components are concerned; it appears, however, that what he considered to be tripolyphosphate was actually a mixture of this and various other acids with longer chains. Indeed, as can be seen from Fig. 1, the maximum of the tripolyphosphoric acid curve is at about 25% whereas a maximum of about 60% was reported by Bell for this member of the series. It is conceivable that tetrapolyphosphoric (4) and probably some acids with longer chains would respond to the same analytical test used in the determination of tripolyphosphoric acid by the Bell (3) method.

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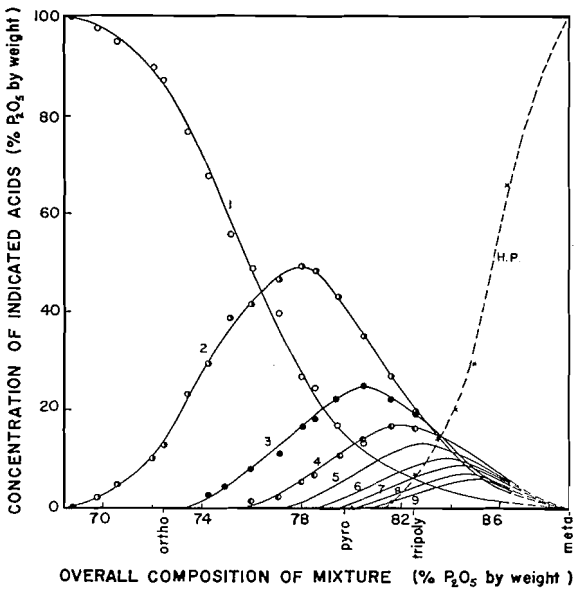

FIG. 1. The composition of the strong phosphoric acids (weight basis); 1 = ortho-, 2 = pyro-, 3 = tri-, 4 = tetra-, 5 = penta-, 6 = hexa-, 7 = hepta-, 8 = octa-, 9 = nona-, and H.P. = "hypoly-".

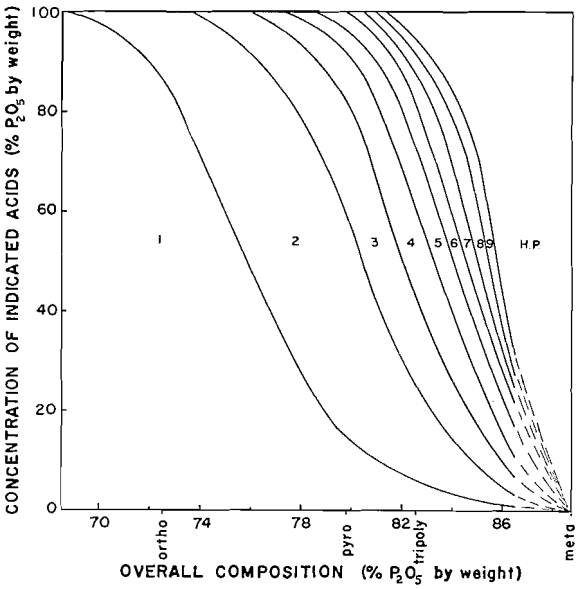

FIG. 2. The composition of the strong phosphoric acids (cumulative) (weight basis); 1 = ortho-, 2 = pyro-, 3 = tri-, 4 = tetra-, 5 = penta-, 6 = hexa-, 7 = hepta-, 8 = octa-, 9 = nona-, and H.P. = "hypoly-".

The "unidentified" acid, believed by him to be a lower polymer of metaphosphoric acid, was found to correspond to the positions of the penta- and hexaphosphoric acids.

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A clear separation from the starting line with complete absence of 'ghosting' was noted up to about 83% phosphorus pentoxide content. This behavior is not found when highly polymerized phosphates are chromatographed; from this it was inferred that the acids analyzed as higher polyphosphoric acids (H.P.) were linear acids with not very long chains.

The acid reported by Bell (3) as "hexametaphosphoric acid", a name originally used by Remziye (30) to describe the acid which coagulated albumin, is not a single species. The line indicated in Fig. 1 by H.P., corresponding to Bell's "hexametaphosphoric acid", has no physical meaning and is given for reference reasons only; it includes all acids with a chain containing more than nine phosphorus atoms. Although at times a good separation was possible up to the dodecapolyphosphoric acid, all the results for reasons of uniformity are reported up to the nonapolyphosphoric acid only.

Thilo and Sauer (35), by applying Ebel's bidimensional technique to the investigation of mixtures of phosphoric acids obtained by dehydration of orthophosphoric acid, have confirmed our observation that only linear polyphosphoric acids were present. Traces of cyclic acids were observed in mixtures containing over 84% phosphorus pentoxide. Any branched members are believed (40) to be very unstable in aqueous solution and will degrade to form linear phosphates before any known analytical method can be applied. It is interesting to note that orthophosphate ion is present to an appreciable extent in the strong phosphoric acids. On the contrary, earlier studies (36, 41) showed that glasses in the sodium oxide – phosphorus pentoxide system contain no detectable amounts of orthophosphate. According to Van Wazer (8, 37) "in the derivation of the theoretical distribution function for these glasses, no orthophosphate appeared, because a single PO_4 group with three negative charges would represent a high charge concentration which would violate the law of detailed distribution of charge". A similar calculation in the case of the acids was inconclusive. However, Van Wazer was able to explain the presence of orthophosphate ions in the acids as follows: "The presence of orthophosphate in the equilibrium mixture of strong phosphoric acids shows that some of the hydrogen atoms are covalently bound to PO_4 groups, so that the monohydrogen orthophosphate ion can be considered as being unionized in these concentrated acids. Naturally this conclusion is in agreement with the very small ionization constant of the $HPO_4^=$ ion in dilute aqueous solution".

Crystallization

The strong phosphoric acid mixtures crystallize upon standing. Rakuzin and Arseniev (29) obtained from a mixture containing 84% phosphorus pentoxide, corresponding to the P_2O_5 content of the pure tetrapolyphosphoric acid, a crystalline product after five days of standing. A description by these authors of the solid obtained indicates that the reported crystals were actually pyrophosphoric acid; this lower-strength acid might have been formed by the absorption of moisture from the air (14).

More careful studies by Gerber and Miles (19), Bell (3), and this laboratory showed that mixtures with a phosphorus pentoxide composition corresponding

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to the P_2O_5 content of pyrophosphoric acid crystallized on standing. The partially crystallized mixture contained more pyrophosphoric acid than the original mixture but, on remelting, the composition returned to that of the original mixture before crystallization.

All methods of investigation, such as crystallization, which involve a change of phase need careful interpretation. It should not be overlooked that the composition of the primary phase separating from a homogeneous phase containing more than one component may bear no relation to the constitution of that phase.

Calculations

By making certain assumptions, it is possible to transform the data of Table III from a weight per cent to a mole per cent basis, and, by using a suitable scale of abscissae, to bring out certain relationships.

The assumptions are:

(*a*) The component acids (and water) can be represented by the general formula $H_{n+2}P_nO_{3n+1}$, where $n = 0, 1, 2, \ldots$. This enables a free water content to be calculated when the component acids can be determined completely. This water is free only in the stoichiometric sense, i.e. it is not combined with P_2O_5 to form a component acid. Probably it is strongly solvated by H_3PO_4, here considered the solvent, since it is the predominant component, and this may account for the simultaneous presence of water and condensed acids in an equilibrium mixture.

(*b*) By extrapolation of calculated "free water" contents, it is assumed that there is no actual "free water" in compositions studied containing more P_2O_5 than the 80.51% mixture. This enables a number average molecular weight to be calculated for the "hypoly" fraction. It neglects the traces of ring compounds present in compositions over 84% phosphorus pentoxide.

The recalculated results are shown in Table IV and are plotted, for the lower acids, in Fig. 3. This figure shows clearly that, as the phosphorus content of the mixture increases, pyrophosphoric acid and "free water" appear before

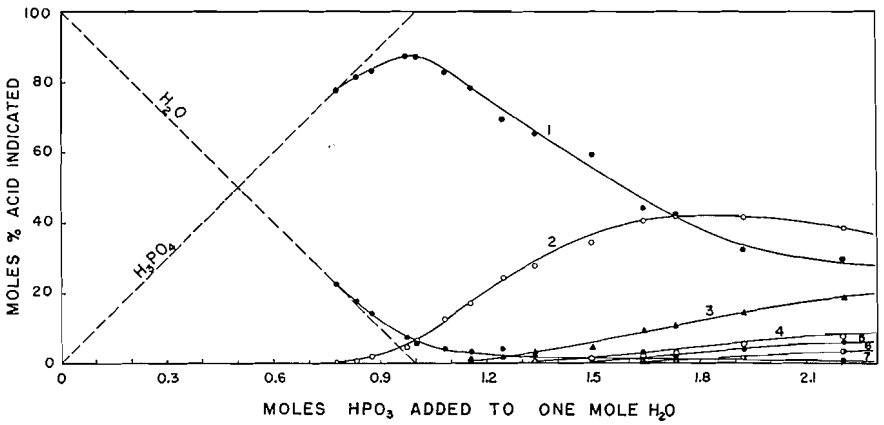

FIG. 3. Computed composition of the strong phosphoric acids (mole basis); 1 = ortho-, 2 = pyro-, 3 = tri-, 4 = tetra-, 5 = penta-, 6 = hexa-, 7 = hepta-.

the over-all composition reaches that of H_3PO_4. At this composition there is only about 88 mole per cent H_3PO_4, with about 6 mole per cent each of "free water" and pyrophosphoric acid. Thus, many of the published properties of "100% H_3PO_4" are subject to a new interpretation.

TABLE IV

COMPOSITION OF STRONG PHOSPHORIC ACIDS
(AND NUMBER AVERAGE CHAIN LENGTH OF "HYPOLY" FRACTION)

Over-all composition (moles HPO_3/mole H_2O)	Composition in terms of component acids and water (mole per cent)											Number average chain length
	$n = 1$	2	3	4	5	6	7	8	9	"Hypoly"	Free water	
0.7773	77.74										22.26	
0.8308	81.29	0.90									17.81	
0.8780	83.60	2.10									14.30	
0.9718	87.35	4.90									7.75	
1.0012	87.61	6.38									6.01	
1.0805	82.88	12.60									4.52	
1.1554	78.30	17.07	1.03								3.61	
1.2447	69.48	24.20	2.20								4.12	
1.3403	65.61	27.99	3.67	0.36							2.37	
1.4952	59.60	34.91	5.56	0.85							−0.92	
1.6397	44.09	40.38	9.21	2.18	0.52						3.64	
1.7310	42.25	41.77	10.54	2.92	0.78						1.74	
1.9269	32.22	41.69	14.18	5.15	1.72	0.62	0.22				4.20	
2.2041	29.61	38.49	18.31	7.70	2.89	1.14	0.89				0.97	
2.5751	21.52	35.97	19.78	11.32	5.86	2.57	1.41	0.77	0.45	0.35		0.9
3.0156	16.48	32.18	17.70	12.93	8.18	4.78	2.96	1.66	1.26	1.87		2.5
3.5765	16.85	28.83	17.96	13.55	8.48	5.51	3.28	2.14	1.12	2.26		—
4.1797	15.17	22.15	16.20	13.65	10.18	6.79	4.89	3.09	2.28	5.60		15.0
5.0519	11.72	17.61	13.03	13.89	10.56	8.11	6.21	4.95	3.38	10.53		14.1
7.8421	12.08	11.65	8.67	10.12	8.35	7.25	3.92	3.25	2.86	31.84		16.3

Figure 3 is also interesting in that it shows that "free water" is present in acid mixtures much higher in phosphorus content than the composition H_3PO_4. When the molecular weight of water, in comparison with the component acids, is considered, a more or less smooth curve for "free water" is obtained, indicating the consistency of the data, until the more complex mixtures are encountered. Here, the analytical difficulties, number of components, and high molecular weights influence the "free water" calculation adversely, although analytical errors in the low molecular weight components may have the greatest effect. Analytical errors which compensated in such a way as not to change the observed number average molecular weight of the component acids would not be detected by this test.

The number average chain lengths calculated for the "hypoly" fraction are shown in Table IV. The inconsistency of the values for the first three mixtures is probably due to the small amounts of the "hypoly" present; however, the number average chain length appears to reach a constant value of about 16 in the rest of the cases, although the amount of "hypoly" increases from 20 to 66% phosphorus pentoxide by weight. Such a maximum might be due to a changing distribution of the molecular weight or the appearance of ring polymers. The latter were not detected chromatographically to any appreciable extent in the compositions analyzed. It is remarkable that the maximum mole per cent is still in the pyrophosphate range, even when about 32 mole per cent of "hypoly" is present. Finally, the general shapes of the curves in Fig. 3 are such that they might be roughly expressed in terms of mass law constants. The average K value, based on concentrations, for the

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second to fifth mixtures in Table IV is 5×10^{-3} (2.43, 4.30, 4.98, 4.99, 8.29 respectively). At most, these indicate some tendency towards a constant value, which might be revealed by more accurate data.

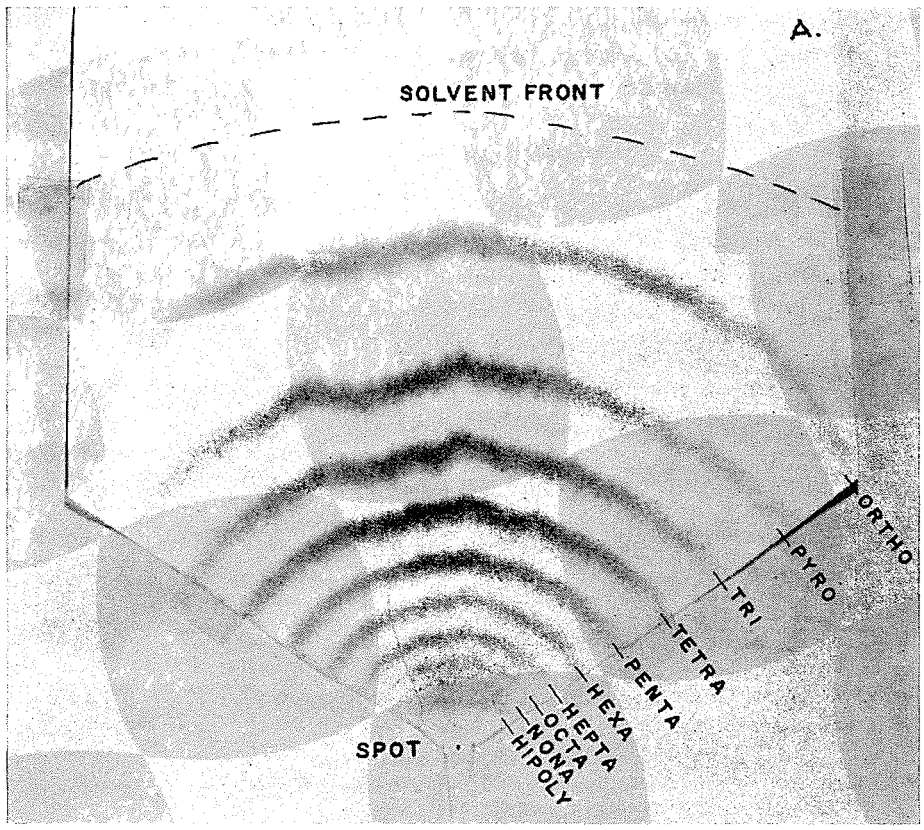

FIG. 4. Chromatographic separation of strong phosphoric acids.

Interpretation

This paper is concerned largely with presenting experimental results. Their interpretation in terms of chemical theory is a matter of much interest. Two methods are suggested by the current literature. First there is the method of Van Wazer (40) based on statistical models which is an application of modern polymer theory; secondly, there is the ionic and mass law method elaborated by Ingold and his school (20) in interpreting their cryoscopic measurements on sulphuric acid in the immediate neighborhood of the 100% sulphuric acid composition. Since the original derivation of the mass law by Guldberg and Waage was based on essentially a statistical argument, these two methods may not be as far apart as appears at first sight. In both cases, the strong phosphoric acids appear to be suitable materials for study.

ACKNOWLEDGMENT

The authors wish to thank Dr. A. E. R. Westman for his interest and help.

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APPENDIX. COMPUTATION METHODS

The calculation of Table IV and the data for Fig. 3 from Table III is simple in principle, involving only stoichiometry and simple assumptions. Involved computations can be avoided by the following methods.

Free Water Content and Mole Percentages (in absence of "hypoly")

For computing purposes, the component acids, and water, can be represented by the formula

$$(H_2O)_{\frac{1}{2}(n+2)}(P_2O_5)_{\frac{1}{2}n}.$$

The computation can then be carried through as illustrated in Table V. Essentially, it involves a comparison, in Column (2), of the total water known to be present in the strong-acid mixture with that computed from the chromatographic analysis, Column (5), which does not include "free water".

TABLE V

(1) Over-all composition (wt. %)	(2)* H_2O	(3) Chromatographic analysis n	(4) Chromatographic analysis P_2O_5	(5) H_2O (4)$\times\frac{n+2}{n}$	(6) Components (4)$\times\frac{2}{n}$	(7)	(8) Moles HPO_3 per mole of H_2O $\frac{2}{(2)-1}$
		Moles per one mole P_2O_5 total				Mole %	
		0			(2) 0.1248	6.4	
H_2O 27.56	2.9976	1	0.8728	2.6184	1.7456	87.4	1.0012
P_2O_5 72.44 (5)	2.8728	2	0.1272	0.2544	0.1272	6.4	
	0.1248		1.0000	2.8728	1.9876	100.0	

**Transferred values have the column of origin indicated in front.*

TABLE VI

(1) Over-all composition (wt. %)	(2)* H_2O	(3) Chromatographic analysis n	(4) Chromatographic analysis P_2O_5	(5) Component acids (4)$\times\frac{2}{n}$	(6) Component acids $\left(\frac{(5)}{(5)\text{ total}}\right)\times 100$	(7) "Hypoly" $\frac{\bar{n}}{\frac{2y}{x-y}}$	(8) Over-all composition $\frac{2}{(2)-1}$
	Moles per one mole P_2O_5 total				(mole %)		(moles)
H_2O 15.80	1.4785	0					H_2O 1.000
P_2O_5 84.20 (4)+(5)	1.2501	1	0.0363	0.0726	15.17		HPO_3 4.179
x	0.2284	2	0.1060	0.1060	22.15		
(4) y	0.2016	3	0.1163	0.0775	16.20		
$x-y$	0.0268	4	0.1305	0.0653	13.65		
		5	0.1217	0.0487	10.18		
		6	0.0975	0.0325	6.79		
		7	0.0819	0.0234	4.89		
		8	0.0592	0.0148	3.09		
		9	0.0491	0.0109	2.28		
		Total	0.7984	0.4517			
		"Hypoly" y	0.2016	(2) 0.0268	5.60	15.0	
				0.4785	100.00		

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Number Average Chain Length of "Hypoly" and Mole Percentages (in absence of "free water")

As illustrated in Table VI, the first part of the computation is the same as in Table V but the water, x, in the "hypoly" fraction is computed rather than "free water", which is assumed to be absent. The component acid formula can now be written $H_2O(HPO_3)_n$. Then, if x moles of water and y moles of P_2O_5 are present in the "hypoly" fraction, $2y$ moles of HPO_3 can be formed, leaving $x-y$ moles of "hypoly" acids. The number average chain length, i.e. the average number of HPO_3 groups per molecule, will then be $2y/(x-y)$.

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ON THE INFRARED ABSORPTION OF WATER AND HEAVY WATER IN CONDENSED STATES[1]

By Paul A. Giguère and K. B. Harvey

ABSTRACT

The infrared spectra (from 2 to 30 μ) of thin films of H_2O and D_2O were measured at various temperatures between 20° and −180°C. A strong absorption band due to the librational mode of the water molecule has its maximum around 710 cm.$^{-1}$ in the liquid. In ice it is shifted to 800 cm.$^{-1}$ at −15°C. and 850 cm.$^{-1}$ at −170°C. The corresponding D_2O bands show the normal isotope shift. Thin films of water pressed between silver chloride plates could not be crystallized even at liquid air temperature as confirmed by their spectra, which were almost identical with those of the liquid.

INTRODUCTION

Water is of considerable importance in infrared spectroscopy for, in addition to being practically omnipresent in nature, it absorbs very strongly over wide regions of the infrared, and it can attack or dissolve many of the salts used as optic materials. In fact the need for cancelling absorption by atmospheric water vapor was largely responsible for such developments as the double-beam and the vacuum spectrometers. On the theoretical side, infrared study of water in various physical states can contribute valuable information on such fundamental problems as the structure of ice, for instance. Whereas the infrared spectrum of the vapor has been studied extensively, the most extensively, no doubt, of all triatomic molecules, those of the condensed phases, although much simpler, are less well known. This is particularly true of the solid for which the only data available on the fundamental vibrations are from the classical work of Fox and Martin (14). These authors could not extend their measurements beyond 7.5 μ, the transmission limit of the fluorite plates which they used to hold the samples. Previously Cartwright (9) had scanned the long wave-length region where he had observed two very broad bands at about 20 μ and 60 μ arising from restricted rotation or "libration" (ν_R) and restricted translation (ν_T) of the water molecule. Existence of these intermolecular vibrations has been anticipated by Bernal (3, 4) and by Ellis (12).

Since then no systematic investigations of these two bands have been reported, at least not for the solid phase.* The early measurements of Rubens and Ladenburg (33) on liquid water were made actually with a soap film. Sohm (35) studied very thin films of liquid (1| micron) in the 15 to 25 μ region where she observed for the ν_R band a series of rounded maxima separated by 52 cm.$^{-1}$ in H_2O and 41 cm.$^{-1}$ in D_2O. This unusual feature must have resulted from interference as it could not be reproduced afterwards (27). More numerous than the infrared are the Raman investigations of liquid water and ice. A number of reviews have been published in the past, the most recent of which is that of Lecomte (21). For comparison, the existing data are

[1]*Manuscript received January 27, 1956.*
Contribution from the Department of Chemistry, Laval University, Quebec, Que.

*Note added in proof.—*In a very recent paper Ferriso and Hornig (J. Chem. Phys. 23: 1464. 1955) mention incidentally an intense band in the infrared spectrum of ice at 812 cm.$^{-1}$ (temperature not stated) from an unpublished thesis by F. P. Reding.*

TABLE I

PREVIOUS DATA ON THE INFRARED AND RAMAN SPECTRA OF ICE

	ν ($cm.^{-1}$)						T, °C.	Ref.
Infrared	160						−10°	9
			1530					
			1644	2222	3256	3790	−9°	14
Raman								
53.5	212				3360		*	32
					3090		−180°	36
					3135			
					3196		*	30, 31
					3321			
	205	601		2225	3126			
					3330		0°	18
	210				3156		0°	11
	213				3147			
52	260				3264		*	25
					3347			
	212						−4°	17

*Temperature not stated.

TABLE II

EXISTING DATA ON THE MOLECULAR SPECTRA OF LIQUID WATER

	ν ($cm.^{-1}$)						T, °C.	Ref.
Infrared		670					*	33
			1615	2130	3300		*	13
	160	500					*	9
						3790	23°	10
		650	1570					
			1645				18°	35
			1649	2146	3382		3°	14
			1646	2128	3395		19°	14
			1642	2092	3426		70°	14
		645		2110		3920	*	27
Raman								
					3200			
60	172	510	1645	2150	3435	3990	*	6
		780			3600			
			1654		3233		*	19
					3433			
					3224			
		550						
		700	1643		3436		*	8
					3625			
	175	500			3150			
		740	1659	2135	3480	4023	12°	24
					3330			
					3530		37°	24
					3670			
					3312			
					3494		67°	24
					3650			
	144	440	1627	2170	3219			
					3445		28°	18
	149	450	1629	2118	3222			
					3460		88°	18
	200		1656	2167	3440	4000	40°	11
					3260			
60	175	475			3426		*	25
		758			3610			

*Not stated; presumably room temperature.

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listed in Tables I and II. A remarkable feature of the Raman spectra is the ν_2 band which seems to be missing in ice as well as in water vapor although it is present, but rather weak, in liquid water. The data on heavy water are quite scanty (Table III); in particular, nothing is available on D_2O ice.

TABLE III

PREVIOUS RESULTS ON THE SPECTRA OF HEAVY WATER (LIQUID)

	ν (cm.$^{-1}$)						T, °C.	Ref.
Infrared			1220	1620	2500		*	13
	170	360					*	9
			1220	1620	2500	2980	*	28
		500	1160 1210				19°	35
Raman	170	500	1207		2389 2509 2366		18°	2
	123 178				2500 2646		*	1
	190	375	1208	1600	2515 2373	2965	50°	11
60	176	375	1207		2539 2670		*	25

**Presumably room temperature.*

Our interest in that question stemmed from a spectroscopic study of the products from water vapor dissociated in the electric discharge (15, 16). Adequate knowledge of the absorption spectrum of ice was, obviously, a prerequisite. Because time was limited and our interest merely incidental only those tests were carried out which required no elaborate preparation nor special equipment. Further work would certainly be desirable, specially in the far infrared, to determine accurately the various frequencies in the acoustical branch of the molecular spectrum of ice. In that respect Raman spectra of single crystals appear more promising than an infrared study of thin, oriented films of ice.

EXPERIMENTAL

The problem of getting thin enough films of water (of the order of a few microns) between insoluble, infrared-transparent plates and at various fixed temperatures down to that of liquid air presented many experimental difficulties. To realize controlled physical conditions an evacuable absorption cell similar to that used for studying the products of dissociated water (16)—minus the discharge tube— was used. The film of water, or heavy water, was held on, or between, 25 mm. salt disks placed in a massive copper block forming the bottom of the coolant well. Kovar or Housekeeper's metal–glass

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seals were found equally suitable, although their average life is rather short despite precautions to minimize the thermal shocks. Heat transfer between the salt windows and the holder was improved by a film of silicone grease in which some finely powdered silver had been dispersed. Alternatively, packing some silver powder tightly around the window gave a slightly better thermal contact but was more tedious. In addition the silver tended to sinter after a few months' use so that it became difficult to remove the salt disk. The temperature of the film was measured with a tiny copper–constantan thermocouple embedded in the salt window. With the absorption cell evacuated the lowest temperature thus attained was −187°C. with liquid nitrogen (−196°) in the coolant well. The spectrometer was a Perkin-Elmer, Model 12C, modified for double pass. A sodium chloride prism covered most of the region investigated, but occasionally lithium fluoride and cesium bromide prisms were necessary. The absorption cell was designed so as to fill almost completely the space between the two spectrometer housings. Thus absorption by atmospheric water vapor was reduced and, at the same time, the cell windows were less likely to fog from condensation.

Several techniques were employed successively in obtaining a suitable film of water. At first a drop of liquid was simply pressed between two polished silver chloride disks. However, this led to the peculiar result that essentially the same absorption spectra were obtained at all temperatures even down to that of liquid air, thereby confirming that no crystallization had occurred (Fig. 1).

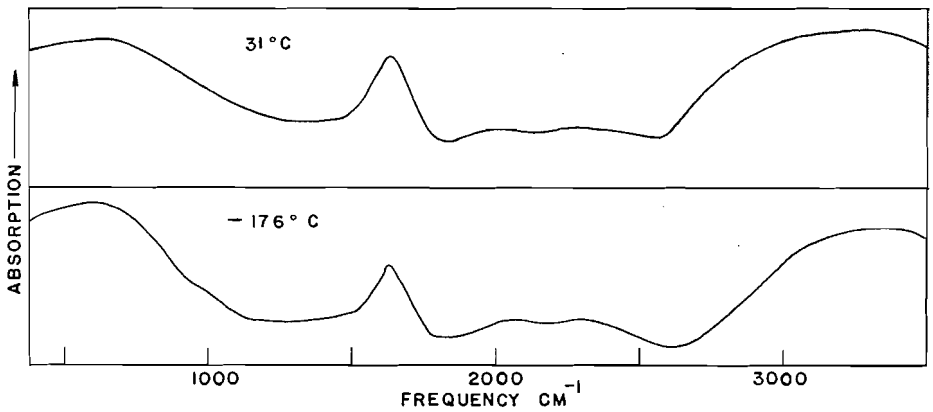

FIG. 1. Infrared absorption spectra of thin films of water between silver chloride plates.

This phenomenon could be repeated any number of times under the same conditions. Next, distillation *in vacuo* of a thin film from a liquid sample onto the salt disk cooled with liquid air was satisfactory at the lower temperatures (Fig. 2), but above −40°C. the infrared radiation of the spectrometer beam resulted in sublimation of the thin film followed by recondensation on the colder parts of the coolant well. Filling the cell with a dry gas did not improve the situation noticeably.

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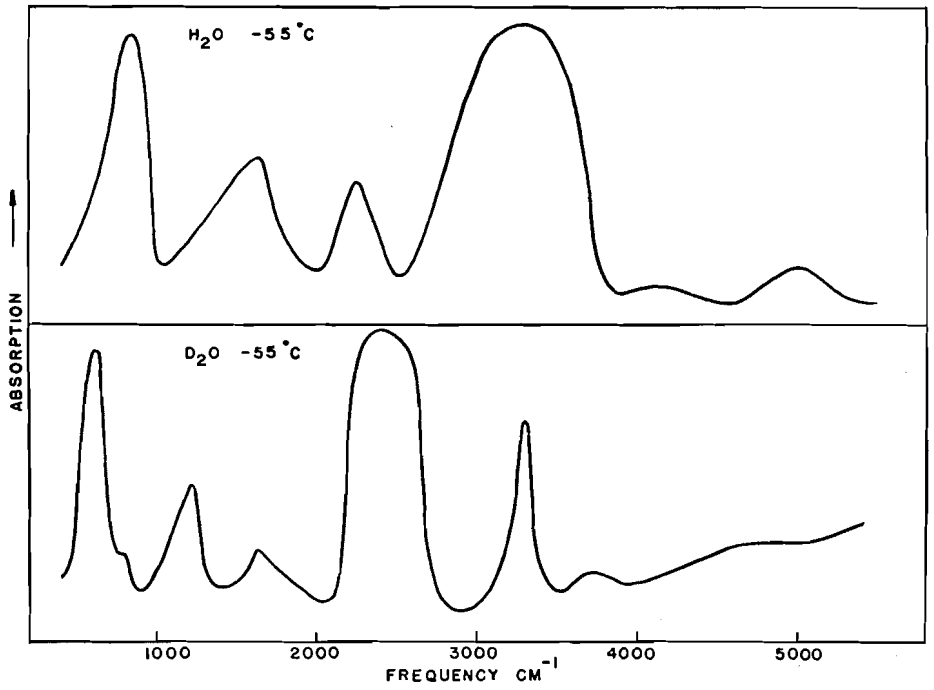

FIG. 2. Composite tracings of the infrared spectra of films of ice and heavy ice condensed on a plate at −55°C. (The weak band at 800 cm.$^{-1}$ and most of the sharp peak at 3300 cm.$^{-1}$ in the spectrum of D_2O ice are due to contamination by traces of H_2O.)

In an attempt to overcome this difficulty a third method was tried. After the film was formed by condensation, as above, the absorption cell was filled with dry gas and taken apart. Previously the coolant had been dumped out in order to prevent condensation of atmospheric water and carbon dioxide on the film. Then the latter was quickly covered with a second window separated by a thin gasket. Following reassembly the cell was evacuated again and the spectra recorded at various temperatures from that of liquid air up. By this stratagem evaporation was prevented but other complications ensued. For instance, the spectra showed considerable scattering at short wavelengths (Fig. 3) owing, no doubt, to coalescence of the microcrystals into larger ones when the film was warmed (temperature not measured but estimated in the order of −40° to −30°C.). That this phenomenon persisted above the melting point of ice is attributed to the formation of minute droplets of water on the non-wetted silver chloride plates.

In the case of heavy water still a different technique had to be developed because the ν_R band in the liquid state extends appreciably beyond 25 μ, the usable limit of silver chloride optics. The sample was placed between two thin sheets of polythene stretched across a cesium bromide window in a demountable liquid cell. Except for lack of rigidity this plastic, in thin sheets, is an excellent material for the 25–35 μ region.

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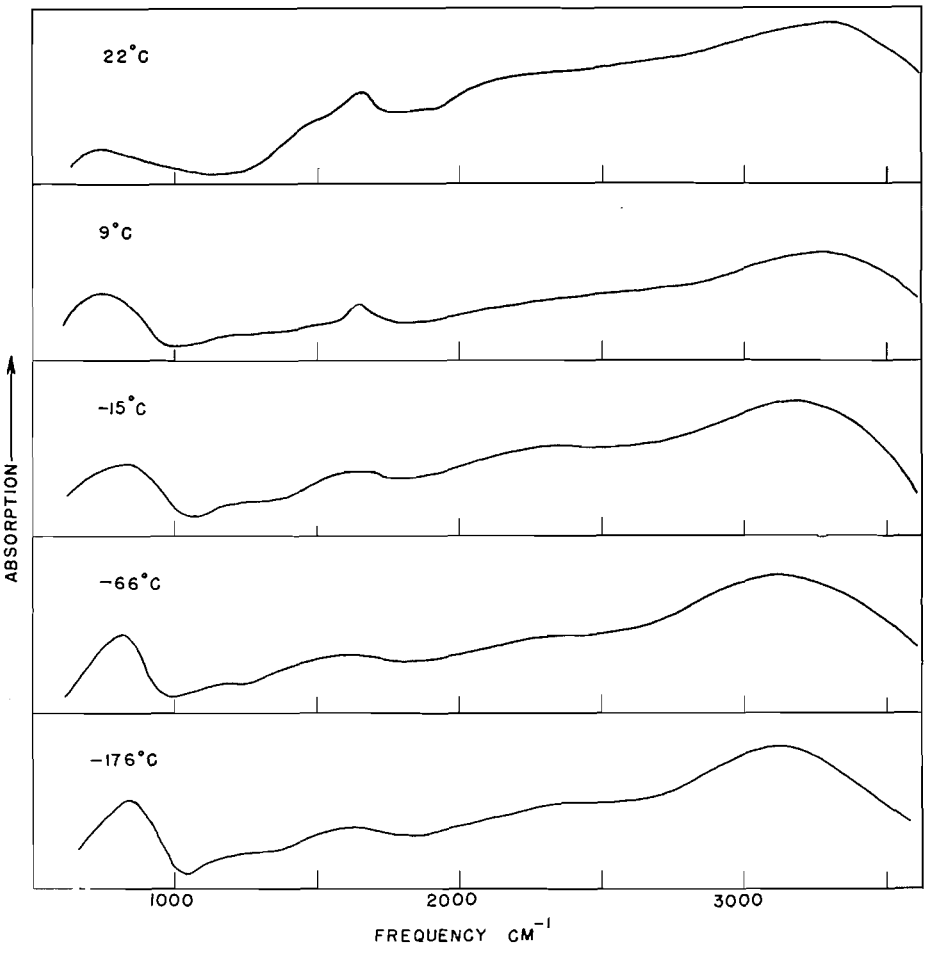

FIG. 3. Effect of temperature on the absorption spectra of thin films of ice condensed on a cold plate.

DISCUSSION OF RESULTS

The new results can best be considered from the two main viewpoints of librational frequency and supercooling of water.

The Librational Frequency

Heretofore the frequency of ν_R in water was not known with any great accuracy owing, mostly, to the flatness and width of the band. Values ranging from 450 to 780 cm.$^{-1}$ (cf. Table II) have been reported for the liquid phase. Some of these estimates were based in part on the frequency of the combination tone, $\nu_2+\nu_R$, at about 2200 cm.$^{-1}$. However, there was a tendency to underestimate the extent of anharmonicity which is quite large, as expected, (some 200 cm.$^{-1}$) on account of the strong interaction of these two deformation modes. The present value, 710 cm.$^{-1}$ is believed correct to $\pm$10 cm.$^{-1}$ on the

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basis of the tracings obtained with the third technique; that is, where the liquid sample was *not* pressed between two salt plates. Indeed, it was observed repeatedly in this work that the ν_R band of compressed films of water was appreciably broader than that of films deposited on a plate. Plyler and Acquista (27) using a film estimated as 0.005 mm. thick have observed an extremely broad band extending from 12 to 40 μ.

As could be surmised, the frequency of ν_R in water is strongly dependent on temperature and physical state. Thus on crystallization it is shifted by about 90 cm.$^{-1}$ towards the shorter wavelengths and the temperature coefficient in ice is fairly large (Table IV). Fox and Martin (14) had found a shift

TABLE IV

PRESENT DATA ON THE INFRARED BANDS OF H_2O AND D_2O IN CONDENSED STATES

Mode	Int.	H_2O				D_2O			
		Liquid 10°	Crystal			Liquid 10°	Crystal		
			−15°	−55°	−170°		−15°	−55°	−170°
ν_R	s.	710	800	820	850	530	590	610	630
$2\nu_R$	v.w.			1500					
ν_2	m.			1650	1650			1210	1210
$\nu_2+\nu_R$	m.			2240	2250			1620	1630
ν_3	v.s.			3240	3260			2440	2450
	v.w.			4150				3295	
	v.w.			5000				3720	

of 75 cm.$^{-1}$ for the combination band $\nu_2+\nu_R$ in fair agreement with our observation since the frequency of ν_2 is little affected by changes of phase. This increase of about 13% in the force constant of ν_R upon crystallization follows from a tightening of the hydrogen bonds (shortening of the O–H . . . O distance). It may be recalled here that Pauling (26) has estimated that 15% of the hydrogen bonds in ice are broken on melting. There are indications in the Raman spectra (Tables I and II) that the other lattice vibration ν_T has a slightly higher frequency in ice than in water.

The value of ν_R in ice is of interest in connection with various physical properties such as specific heat and zero-point energy of the lattice. Twenty years ago Bernal and Tamm (4) calculated the librational frequency from the ice model of Bernal and Fowler (3) and thus arrived at a much lower result, 475 cm.$^{-1}$. From this they estimated the difference of the heats of vaporization of H_2O and D_2O ices to be 0.35 kcal./mole at the melting points. This is now known to be 0.46 kcal./mole (20), not 0.32 as was then believed on the basis of extrapolated data for the vapor pressure of D_2O (22). More recently Blue (5) has calculated an approximate value of ν_R in the temperature region below the melting point. His method, which rests on the difference between the measured heat capacity of ice and heavy ice, also leads to a somewhat lower result than ours, namely 660 cm.$^{-1}$ (723 cm.$^{-1}$ when hindered translation is

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taken into account).* From an analysis of the three modes of libration around each of the principal axes of the molecule Blue has concluded that the three frequencies should differ among themselves by less than 10% for ice and less than 20% for heavy ice. Another conclusion from his analysis is that the librational frequencies decrease with rising temperature. Our results do show an appreciable decrease in frequency. It is doubtful, however, if the effect becomes much larger near the melting point of ice.

Although they did not attempt to locate the maximum of the broad, flat ν_R bands in the Raman spectra of H_2O and D_2O, Cross *et al.* (11) deduced from their analysis of the structure of ice that it should have a frequency of the order of 700 to 900 cm.$^{-1}$. The present figure, exactly halfway in that range, is further evidence for the soundness of their perturbation treatment of the water molecule.

The Supercooling of Water

The persistence of the liquid-type absorption spectra of thin films of water down to liquid-air temperature (Fig. 1) was unexpected. The frequency of ν_R provided a reliable criterion for this, as the other bands are either too broad or little affected by phase changes. Previous instances have been reported of thin films of water in a non-crystalline state at very low temperatures (7, 23, 29). In all these cases, however, the samples were cooled very quickly and they usually crystallized on being warmed above a certain temperature. Our films of water pressed between silver chloride plates could be warmed and cooled over a wide temperature range without significant alteration in their spectra. Fox and Martin (14) obtained crystalline films of ice at −9°C. by "jolting" the absorption cell. We confirmed that thin films of water between fluorite plates become rigid quite readily around −10° simply by moving one plate with respect to the other. Our experimental arrangement did not make this test possible at liquid air temperature but on the other hand jolting or tapping the sample holder never induced crystallization at that temperature. The difference, no doubt, comes from the fact that under such conditions our samples were well below the temperature range of maximum rate of nucleation in supercooled water.

The recent work of Pryde and Jones (29) has thrown new light on the low-temperature forms of water-substance. In particular they have confirmed the observations of Simon (34) that vitreous (or glassy) water has an appreciably smaller heat capacity than supercooled water (Fig. 4) and in one experiment they were able to follow the reversible transition, near −147°C. (T_g), in a finely subdivided sample of water held in a porous copper block. On the other

Some of the Raman data quoted by this author in comparison with his calculated results were misinterpreted. The "strong sharp line at about 600 cm.$^{-1}$" in the spectra published by Cross, Burnham, and Leighton (11) was not identified by them with the librational motion. In fact this band is much too sharp for an O–H vibration in condensed phases. Furthermore, it appears unchanged in the Raman spectra of both liquid and *solid* H_2O and D_2O *(Figs. 2 and 3 of Ref. 11). Undoubtedly it was due to an unfiltered line in the mercury–argon discharge used for that work, presumably the 2576.29 Å line arising from the* $6s6p^3P_1$–$6s9s^3S_1$ *transition of the mercury atom. (Private communication from Prof. Leighton.) The same phenomenon may have occurred in Hibben's work (18), although there the situation is not so clear.*

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hand the material formed by condensation from the vapor into calorimeters cooled in liquid oxygen, although it appeared transparent, was only partly vitreous because it always crystallized irreversibly at a fixed temperature, 129°±1°C. From the heat evolved the vitreous fraction was estimated to range from one-twentieth to one-third, depending on the thickness and the rate of formation of the layers.

The present results seem to fit well into that picture. Indeed, the thin films condensed from water vapor did look glassy at liquid air-temperature but they turned snowy white in the vicinity of −120°C. That the infrared spectrum remained unchanged thereupon (Fig. 3) may be due to either or both of the following causes: (*a*) the films were largely crystalline to begin with or (*b*) the absorption spectrum of vitreous water is similar to that of ice but different from that of the supercooled liquid. The latter view appears logical considering the large contribution of intermolecular vibrations to the heat capacity of condensed phases (Fig. 4). In the X-ray experiments of Burton and Oliver (7)

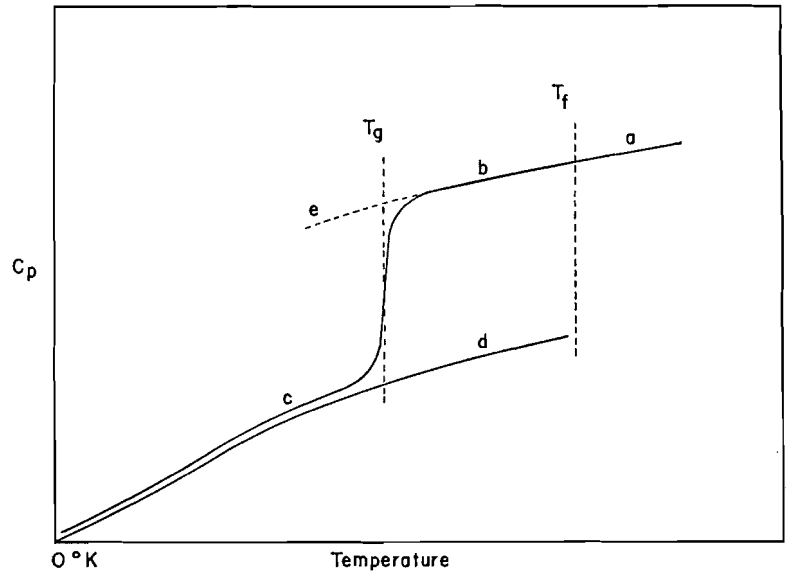

FIG. 4. Specific heat – temperature curves, after Simon (34), for a substance in the following states: (*a*) liquid, (*b*) supercooled liquid, (*c*) glass, (*d*) crystal, and (*e*) equilibrium curve for supercooled liquid.

water vapor condensed on surfaces colder than −110° was found to be vitreous while above −80° ice was obtained. Between these two temperatures crystallization would take place only along certain crystallographic planes. Since their samples were prepared extremely slowly and at very low pressures (10^{-4} mm. Hg) the heat of condensation was quickly dissipated, an essential condition for glass formation. Our attempts to repeat their experiments were unsuccessful (the films were in all cases crystalline) presumably because evaporation was carried out at a much higher pressure (5×10^{-2} mm. Hg).

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Another factor may be that silver chloride is a poorer heat conductor than metallic copper used by Burton and Oliver for holding their samples.

No estimate of the absorption coefficients of the various bands will be attempted here since the thickness of the films was not measured. The matter is further complicated by the scattering and broadening phenomena mentioned above. Qualitatively speaking the intensity of the 6 μ band in ice decreases on cooling while that of the 3 μ band increases (Fig. 3). The same trend had already been noticed in liquid water (14). From Fig. 1 it seems that this effect is much less pronounced in the vitreous state. As for the ν_R band, it is not only sharper, but also stronger in ice than in liquid water.

ACKNOWLEDGMENT

The authors are grateful to the Consolidated Mining and Smelting Co. of Canada for a research fellowship granted to one of them (K. B. H.), and to the National Research Council for generous financial assistance.

RÉSUMÉ

On a mesuré l'absorption infrarouge (de 2 à 30 μ) de l'eau ordinaire et de l'eau lourde dans les états liquide et solide. La libration, ou rotation gênée des molécules, donne naissance à une forte bande d'absorption aux environs de 710 cm.$^{-1}$ dans l'eau liquide. Dans la glace cette bande se retrouve vers 800 cm.$^{-1}$ au voisinage du point de fusion et vers 850 cm.$^{-1}$ à la température de l'air liquide. Les fréquences correspondantes dans l'eau lourde sont à 530, 590 et 630 cm.$^{-1}$. On a constaté que dans le cas de minces films d'eau retenus entre deux plaques polies de chlorure d'argent le spectre demeure essentiellement le même lorsqu'on refroidit jusqu'à -180°C., ce qui indiquerait l'absence de cristallisation.

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THE DETERMINATION OF PARTIAL SPECIFIC VOLUMES BY DIFFERENTIAL SEDIMENTATION[1]

By W. G. Martin, W. H. Cook, and C. A. Winkler[2]

ABSTRACT

Sedimentation in aqueous and heavy water solutions has been used to determine the partial specific volume of bovine plasma albumin, sodium alginate, and polyvinyl alcohol, resulting in 0.74 ± 0.01 (S.D.), 0.54 ± 0.06, and 0.79 ± 0.01 ml./gm. at 25°C., respectively. The sedimentation method yields results comparable with those given by conventional methods for macromolecules.

INTRODUCTION

The estimation of molecular weight by sedimentation requires a knowledge of the partial specific volume of the sedimenting material. With purified protein preparations a satisfactory value of the partial specific volume, $\bar{V}$, can often be assumed from published results. However this is not possible for macromolecules that have not been extensively studied. The classical pycnometer (19) and float (6) methods require more material than may be available and the density gradient column (11) has limitations when applied to such materials as lipoproteins.

McBain (14) postulated that $\bar{V}$ of macromolecules could be estimated from their differential sedimentation rate in media of differing density. Obviously such estimates will be subject to the combined errors of at least two sedimentation determinations and these will be in general greater than the errors applicable to the classical methods of determining density. The classical methods, however, are far more sensitive than the sedimentation method to errors in concentration or residual hydration and small percentages of impurities. Such errors are inevitable with macromolecules that have a great affinity for water, decompose at elevated temperatures, or associate with other substances. The sedimentation method is attractive, therefore, since it is less subject to the errors often inherent in the material itself and since it requires only a small sample.

Evaluation of $\bar{V}$ of macromolecules by the sedimentation method has been made from experiments in which glycerol, sucrose, serum albumin, or deuterium oxide (4, 12, 13) was used to vary the density of the sedimentation medium. Although the range of density obtainable with deuterium oxide is limited, it can be assumed to behave in the same manner as water and thus avoids the uncertainties of differential interaction between solvent and solute inherent in the use of other materials. With the exception of polystyrene latex spheres, previous experiments with deuterium oxide were made on materials of uncertain physical characteristics.

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In the present study sodium alginate (AC_1), bovine plasma albumin (BPA), and polyvinyl alcohol (PVA) were selected as a typical polyelectrolyte, globular protein, and linear polymer, respectively, and their sedimentation rates in aqueous and heavy water media were measured.

THEORY

From the theory of particle sedimentation in high centrifugal fields, Svedberg (19) developed the relation:

$$[1] \qquad fs = M(1-\bar{V}\rho)$$

where f, s, M, and $\bar{V}$ are respectively the frictional coefficient, sedimentation coefficient, molecular weight, and partial specific volume of the macromolecule and ρ is the density of the sedimentation medium.

The frictional coefficient f in equation [1] is obviously a function of the shape and effective volume of the molecule in solution and also of the viscosity of the solvent. Corrections can be made for viscosity differences, to permit the use of a frictional coefficient independent of solvent viscosity defined by the equation:

$$[2] \qquad f = f^1\eta.$$

It is reasonable to assume that there will be no significant differences in molecular shape and effective volume of macromolecules in aqueous and heavy water media (18). Again little effect upon electrostriction would be expected. However, a significant and rapid exchange of deuterium atoms for labile hydrogen atoms (10, 17) of macromolecules will occur in solutions containing deuterium oxide. The result will be an increase in molecular weight and since the volume of the macromolecules does not change, $\bar{V}$ will decrease. Thus M in aqueous solution will become Mk in deuterium oxide and $\bar{V}$ will change to $\bar{V}/k$, where k is the ratio of the molecular weights in the two media. Some preliminary measurements of $\bar{V}$ in aqueous and heavy water solutions indicated that $\bar{V}$ was lower in the latter solvent (15).

The sedimentation in aqueous and heavy water solutions may therefore be expressed as:

$$[3] \qquad f^1\eta_1 s_1 = M(1-\bar{V}\rho_1),$$

$$[4] \qquad f^1\eta_2 s_2 = Mk(1-\bar{V}\rho_2/k).$$

Dividing equation [3] by equation [4] and rearranging,

$$[5] \qquad \bar{V} = (\eta_2/\eta_1 - k\, s_1/s_2)(\rho_1\eta_2/\eta_1 - \rho_2 s_1/s_2)^{-1}.$$

The standard error of $\bar{V}$ can be approximated from the observed standard errors of s_1 and s_2 by the conventional device of regarding mathematical differentials as statistical differentials. Partial differentiation of equation [5] results in:

$$[6] \qquad \partial\bar{V}/\partial s_i = Fs_j$$

where $i = 1$ when $j = 2$ and vice versa, and where $F = (k\rho_1 - \rho_2)\eta_1\eta_2/(\rho_1 s_2\eta_2 - \rho_2 s_1\eta_1)$. Now assuming that η and ρ have negligible errors, that s_1 and

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s_2 have the same small proportional error, and that the joint fractional error of s_1 and s_2 is the root-sum-square of the individual errors, equation [6] can be transformed to give:

$$[7] \qquad \Delta\bar{V} = F(s_1^2\Delta^2 s_2 + s_2^2\Delta^2 s_1)^{\frac{1}{2}}$$

where Δ is to be read "the standard error of".

EXPERIMENTAL

Material

Crystalline BPA (Armour) was used without further purification. The PVA (Shawinigan Chemicals Ltd.) and AC_1 (Alginate Industries Ltd.) were dissolved in distilled water, filtered or centrifuged to remove any insoluble material, and then lyophilized. Weighed amounts of AC_1 were redissolved in measured volumes of buffer solution and again lyophilized. Each material was stored over P_2O_5 *in vacuo*.

The BPA and PVA were caused to sediment in 0.2 μ sodium chloride solution and dilutions were made by adding solvent to a stock solution. Known weights of the lyophilized AC_1 were dissolved in the calculated weight of solvent and sedimentation was in 0.15 μ sodium phosphate – sodium chloride buffer at pH 6.6. Some solutions of each material were made directly by weight.

Methods

The densities of the heavy water and heavy water solutions were measured mainly in the density gradient column at 25°C. Some of the measurements on the heavy water and all of the density measurements of the aqueous solutions were made with a small magnetic float (15). The stock solution of deuterium oxide had a density of 1.039 gm./ml. but that used for making the solutions following storage in secondary stock bottles varied from 1.035 to 1.039 gm./ml.

The viscosity of the deuterium oxide as determined in an Ostwald-Fenske viscometer was 1.099 centipoise at 25.0°C. Viscosities of the salt solutions were obtained from the solvent viscosities plus the increments due to the salts, calculated from Svedberg's tables (19).

Sedimentation experiments were made with the Spinco ultracentrifuge in a 12 mm. cell at 59,780 or 52,640 r.p.m. with a few experiments at lower concentrations in a 30 mm. cell at 50,740 r.p.m. The intercepts at zero concentration in aqueous medium for AC_1 and BPA were calculated from published data (5, 16, 21). The data were corrected for the drop in rotor temperature with acceleration (2, 22) unless, as in some experiments, the temperature was controlled by a rotor temperature indicator and control unit. The experiments were made at approximately 25°C. and the sedimentation coefficients were corrected to 25°C. by multiplying by η_t/η_{25}, where η refers to the viscosity of the sedimentation medium (1).

The accepted values of $\bar{V}$ for BPA and PVA were taken from the literature (6, 7, 8, 20) but the value for AC_1 was redetermined with a float apparatus similar to that of MacInnes (6). For this determination the refractive index increment of sodium alginate (5) of 152×10^{-5} gm.$^{-1}$ dl.$^{-1}$ was used to estimate concentration.

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RESULTS AND DISCUSSION

Extrapolation of the experimental data to zero concentration minimizes errors arising from concentration dependence and hydration and enables the solvent viscosity to be used in correcting to standard conditions. The $S^{\circ}_{25,\ \text{medium}}$ values were calculated from the intercepts of Fig. 1. The relation

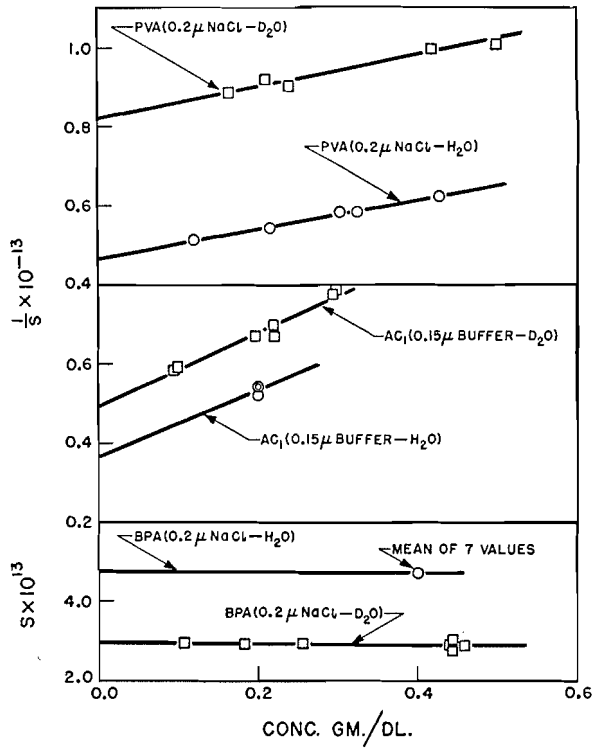

FIG. 1. Concentration dependence of the sedimentation coefficients of bovine plasma albumin, sodium alginate, and polyvinyl alcohol, in aqueous and heavy water media at 25°C.

between sedimentation coefficient and concentration was linear for BPA but a plot of $1/S$ vs. C was necessary to obtain a linear relation for PVA and AC_1. The lines in Fig. 1 were fitted by the method of least squares.

The results are summarized in Table I. The reported $\bar{V}$ values were computed by equation [5]. From the amino acid composition of BPA (9), the number of labile hydrogen atoms was estimated, and k was calculated. Similarly the number of labile hydrogen atoms in each repeating unit of AC_1 (3) and PVA (8) was used to calculate k for these macromolecules.

The value of 0.74 ± 0.01 (S.D.) for $\bar{V}$ of BPA is satisfactory, as it shows a small random error and is in good agreement with the value of 0.734_3 determined with MacInnes float equipment (6).

The partial specific volume of 0.54 ± 0.06 found for AC_1 shows a relatively high experimental error and is considerably higher than the value of 0.481 ± 0.003 obtained at four concentrations with the MacInnes apparatus in this

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TABLE I

DATA AND CALCULATION OF $\bar{V}$

	BPA in 0.2 μ NaCl		AC_1 in 0.15 μ buffer		PVA in 0.2 μ NaCl	
	H_2O	D_2O	H_2O	D_2O	H_2O	D_2O
S^0_{25}, medium, svedberg units	4.78±0.04	2.97±0.03	2.76±0.06	2.02±0.05	2.14±0.03	1.22±0.03
η_{25}, medium, cp.	0.912	1.117	0.919	1.124	0.912	1.117
ρ_{25}, medium, gm./ml.	1.005	1.112	1.004	1.111	1.005	1.113
k		1.016		1.011		1.023
$\bar{V}$ (equation [5]), ml./gm.	0.74±0.01		0.54±0.06		0.79±0.01	
$\bar{V}$ (conventional methods)	0.734_3 (6)		0.481±0.003		0.765 (8) 0.748±0.005 (7) 0.762±0.003 (20)	

investigation. However, the latter value may be subject to somewhat greater total error since the concentration was determined from the refractive index increment. An error of 1% in estimating concentration could result in an error in $\bar{V}$ of 0.005. Considering the magnitude of the random and possibly bias errors, the difference in $\bar{V}$ might not be important.

From the literature, $\bar{V}$ of PVA was 0.765 (8), 0.748±0.005 at 25°C. (7), and 0.762±0.003 at 25°C. (20). The value of 0.79±0.01 at 25°C. by the sedimentation method is high, but does not differ significantly from the other values.

Thus, $\bar{V}$ of the macromolecules obtained by sedimentation in aqueous and heavy water media is comparable with $\bar{V}$ obtained by classical methods. The sedimentation method would be especially useful for material in short supply, of uncertain concentration, or both.

ACKNOWLEDGMENT

The authors wish to express their thanks to Dr. P. A. Charlwood for assistance with the MacInnes apparatus, to Mr. N. T. Gridgeman for aid in estimating the errors involved, and to Atomic Energy of Canada Limited for the supply of heavy water.

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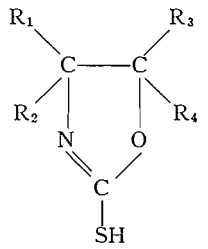
THE STRUCTURES AND CHEMISTRY OF THE PRODUCTS FROM THE REACTION OF AMINO ALCOHOLS WITH CARBON DISULPHIDE[1]

By M. Skulski, D. L. Garmaise, and A. F. McKay

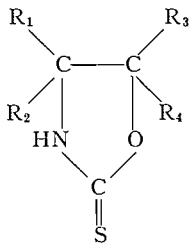
ABSTRACT

A study of the infrared spectra of the oxazoline derivatives, which are formed by the condensation of carbon disulphide with amino alcohols, shows that they possess the oxazolidine-2-thione structure rather than the tautomeric 2-thiol-2-oxazoline structure. 2-Benzylamino-4,4-dimethyl-2-oxazoline was formed by the reaction of benzylamine with 2-methylmercapto-4,4-dimethyl-2-oxazolinium iodide. 5-Diethylaminomethyl-2-oxazolidone and its methylation product also have been prepared.

The structures of the oxygen–nitrogen containing heterocyclics from the reaction of carbon disulphide with amino alcohols have been described previously as either oxazoline-2-thiols (I) (2, 8) or oxazolidine-2-thiones (II) (4, 5). Structure I is encountered most frequently in the literature (8) although Ettlinger (3) describes the infrared spectra of oxazolidine-2-thione and 5,5-dimethyloxazolidine-2-thione in detail. A further study of the infrared spectra



I



II

(Table I) of several of these heterocyclics and their corresponding methylation products confirms structure II as the correct one for these condensation

TABLE I

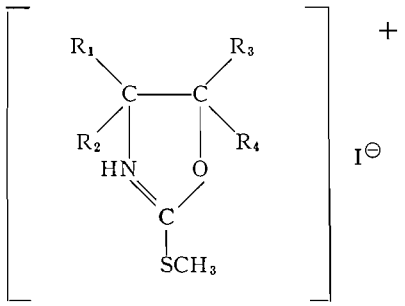
Infrared absorption band of substituted oxazolidine-2-thiones

Compound	N—H stretching	C=N	N—H bending
4-Methyl-4-hydroxymethyloxazolidine-2-thione	3380[a]		1526
	3265[a]		
	3145		
4,4-Dimethyloxazolidine-2-thione	3155		1525
5-Diethylaminomethyloxazolidine-2-thione	3140		1546
2-Methylmercapto-4,4-dimethyl-2-oxazolinium iodide	3275	1646	1533
	3030		
2-Methylmercapto-4-ethyl-2-oxazolinium iodide	3315	1641	1528

[a]*One of these bands may be the result of O—H stretching vibrations.*

[1]*Manuscript received February 3, 1956.*
Contribution from the L. G. Ryan Research Laboratories of Monsanto Canada Limited, Ville LaSalle, Quebec.

products. The infrared spectra of 4-methyl-4-hydroxymethyloxazolidine-2-thione (II, $R_1 = CH_3$; $R_2 = HOCH_2$; R_3 and $R_4 = H$), 4,4-dimethyloxazolidine-2-thione (II, R_1 and $R_2 = CH_3$; R_3 and $R_4 = H$), and 5-diethylaminomethyloxazolidine-2-thione (II, R_1, R_2, and $R_3 = H$; R_4 = diethylaminomethyl) show the absence of a C=N band and the presence of strong N—H stretching and bending bands. On the other hand 2-methylmercapto-4,4-dimethyl-2-oxazolinium iodide (III, R_1 and $R_2 = CH_3$; R_3 and $R_4 = H$) and 2-methylmercapto-4-ethyl-2-oxazolinium iodide (III, R_1, R_3, and $R_4 = H$; $R_2 = C_2H_5$) do have strong C=N stretching bands at 1646 cm.$^{-1}$ and 1641 cm.$^{-1}$ respectively in agreement with their structure (III).



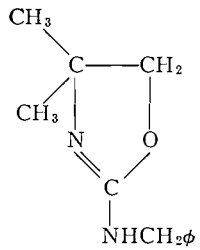
III

The yields of the substituted oxazolidine-2-thiones with the exception of 4-methyl-4-hydroxymethyloxazolidine-2-thione are based on the following equation:

$$2NH_2CR_1R_2CR_3R_4OH + CS_2 \rightarrow HOCR_3R_4CR_1R_2NHCS_2^{\ominus}\overset{\oplus}{N}H_3CR_1R_2CR_3R_4OH$$
$$\xrightarrow{\Delta} II + NH_2CR_1R_2CR_3R_4OH + H_2S.$$

The yield of 4-methyl-4-hydroxymethyloxazolidine-2-thione was raised to 84.7% (based on conversion of 1 mole equivalent of amino alcohol into 1 mole equivalent of the substituted oxazolidine-2-thione) by intermittent refluxing of the reaction mixture with additional portions of carbon disulphide.

2-Methylmercapto-4,4-dimethyl-2-oxazolinium iodide was converted into 2-benzylamino-4,4-dimethyl-2-oxazoline (IV) by refluxing with benzylamine in the presence of ethanol. This reaction is similar to the conversion of 2-



IV

methylmercapto-2-imidazolines into 2-substituted amino-2-imidazolines previously (1, 7) described.

During the course of this work 5-diethylaminomethyl-2-oxazolidone (m.p. 51.5–53°C.) and 5-(diethyl methyl ammonium methyl)-2-oxazolidone iodide (m.p. 160.5–161.5°C.) also were prepared.

EXPERIMENTAL[2]

4,4-Dimethyloxazolidine-2-thione (6, 8)

2-Amino-2-methyl-1-propanol (44.6 gm., 0.5 mole) in benzene (150 cc.) was added dropwise to a stirred solution of carbon disulphide (35.3 gm., 0.55 mole) in benzene (150 cc.) at 5°C. over a period of 15 min. The stirring was continued for 30 min. at room temperature after which the yellow crystalline intermediate was recovered by filtration. This dithiocarbamate salt was heated in an oil bath at 105–135°C. until the evolution of hydrogen sulphide ceased. The cooled residue was triturated with water (100 cc.) and the colorless crystals (m.p. 121–123°C.) were removed by filtration, yield 24.7 gm. (75.3%). Two crystallizations from water raised the melting point to 123.5–124°C. Calc. for C_5H_9NOS: C, 45.77; H, 6.91; N, 10.68%. Found: C, 45.58; H, 6.60; N, 10.3%.

2-Methylmercapto-4,4-dimethyl-2-oxazolinium Iodide

4,4-Dimethyloxazolidine-2-thione (20 gm., 0.15 mole) was refluxed in a solution of methyl iodide (23.8 gm., 0.16 mole) in absolute methanol (70 cc.) for 30 min. On cooling in a freezing mixture, colorless crystals (m.p. 80–82°C.) were obtained, yield 25.2 gm. (57.3%). The melting point was raised to a constant value of 84–85°C. by one crystallization from cold absolute methanol. Calc. for $C_6H_{12}INOS$: C, 26.38; H, 4.43; S, 11.74; N, 5.13%. Found: C, 26.67; H, 4.15; S, 11.45; N, 4.94%.

2-Benzylamino-4,4-dimethyl-2-oxazoline

A solution of 2-methylmercapto-4,4-dimethyl-2-oxazolinium iodide (25.15 gm., 0.09 mole) and benzylamine (9.87 gm., 0.09 mole) in ethanol (10 cc.) was refluxed for eight and a half hours. Removal of the ethanol *in vacuo* under an atmosphere of nitrogen gave a turbid oil (yield 30 gm.). A small sample of this oil was converted into its picrate (m.p. 149–150°C.) in the usual manner. Two crystallizations from ethanol raised the melting point to 150–151°C. Calc. for $C_{18}H_{19}N_5O_8$: C, 49.86; H, 4.42; N, 16.15%. Found: C, 49.54; H, 4.39; N, 16.3%.

The major portion (27.76 gm.) of the oily reaction product was dissolved in warm (50°C.) water (500 cc.) and the solution was passed through a column of Amberlite IRA-400 resin (300 cc.) at a rate of 7–8 cc. per min. The column was washed with 8500 cc. of water. Colorless needles (m.p. 73–73.5°C.) were obtained in 55.5% yield (11.5 gm.) from the effluent and washings on evapora-

[2]*All melting points are uncorrected. Microanalyses were determined by Micro-Tech Laboratories, Skokie, Illinois, and Drs. G. Weiler and F. B. Strauss, Oxford, England.*

tion *in vacuo* under nitrogen. Two crystallizations from carbon tetrachloride raised the melting point of the 2-benzylamino-4,4-dimethyl-2-oxazoline to 79–80.5°C. Calc. for $C_{12}H_{16}N_2O$: C, 70.53; H, 7.89; N, 13.72%. Found: C, 70.81; H, 7.83; N, 13.78%.

4-Ethyloxazolidine-2-thione

4-Ethyloxazolidine-2-thione (m.p. 73–74°C.) (8) was prepared from 2-amino-1-butanol by the method described above for 4,4-dimethyloxazolidine-2-thione. Calc. for C_5H_9NOS: C, 45.77; H, 6.92; N, 10.68; S, 24.44%. Found: C, 45.92; H, 6.47; N, 10.5; S, 24.8%.

2-Methylmercapto-4-ethyl-2-oxazolinium Iodide

A solution of 4-ethyloxazolidine-2-thione (4 gm., 0.03 mole) and methyl iodide (4.33 gm., 0.03 mole) in 35 cc. of absolute methanol was refluxed for 30 min. The residue, after removal of the methanol *in vacuo*, crystallized on standing, yield 3.91 gm. (43.4%). Crystallization from absolute methanol raised the melting point from 83–84.5°C. to 84.5–85.5°C. Calc. for $C_6H_{12}INOS$: C, 26.38; H, 4.43; N, 5.13%. Found: C, 26.27; H, 4.44; N, 5.12%.

4-Methyl-4-hydroxymethyloxazolidine-2-thione

Carbon disulphide (83.75 gm., 1.1 mole) was added to a stirred solution of 2-amino-2-methyl-1,3-propanediol (105.1 gm., 1 mole) in ethanol (750 cc.) at 2–5°C. over a period of 25 min. This solution was refluxed for six hours after which a second portion of carbon disulphide (42 gm., 0.55 mole) was added and the refluxing continued for another 16 hr. Finally a third portion (80 gm., 1.05 moles) of carbon disulphide was added and the solution was refluxed for a further 16 hr. After removal of the excess carbon disulphide and solvent, a brown semicrystalline residue was obtained. It was triturated with acetone and the colorless crystals (m.p. 88–93°C.) were removed by filtration, yield 124.5 gm. (84.7%). The crude material was purified to a constant melting point of 92.5–93.5°C. by several crystallizations from ethyl acetate. Calc. for $C_5H_9NO_2S$: C, 40.79; H, 6.16; N, 9.52; S, 21.79%. Found: C, 40.95; H, 6.73; N, 9.65; S, 21.6%.

A portion (19.5 gm., 0.13 mole) of the 4-methyl-4-hydroxymethyloxazolidine-2-thione was refluxed in absolute methanol (75 cc.) with methyl iodide (20.7 gm., 0.146 mole) for 30 min. Removal of the alcohol *in vacuo* under nitrogen gave a yellow crystalline product (m.p. 112–114.5°C.), yield 13.76 gm. (79.2%). Crystallization from ethyl acetate raised the melting point to 115.5–116.5°C. This material gave a negative qualitative test for sulphur and its analytical values agreed with those calculated for 4-methyl-4-hydroxymethyl-2-oxazolidone. Homeyer (5) reported the melting point of this compound as 115–116.5°C. Calc. for $C_5H_9NO_3$: C, 45.80; H, 6.92%. Found: C, 45.68; H, 6.74%.

5-Diethylaminomethyloxazolidine-2-thione

A solution of 1-amino-3-diethylamino-2-propanol (219.4 gm., 1.5 moles)

in 1000 cc. of benzene was added dropwise to a stirred solution of carbon disulphide (125.6 gm., 1.65 moles) in 1750 cc. benzene at 2°C. over a period of four hours. After 15 min., a grayish precipitate formed. The reaction mixture was allowed to stand overnight in the refrigerator after which the solid material was removed by filtration. This solid was suspended in 3000 cc. of ethanol and the solution was refluxed until the evolution of hydrogen sulphide ceased. The resulting brown ethanol solution was filtered to remove sulphur and then treated with Norite A. The filtrate, on evaporation to one-third its original volume and cooling, gave colorless needles. A second crop was obtained from the mother liquor. The total yield of crude product (m.p. 95–97°C.) was 109 gm. (77.2%). This crude material after crystallization from ethanol melted at 96–97°C. Calc. for $C_8H_{16}N_2OS$: C, 51.02; H, 8.57; N, 14.86; S, 17.03%. Found: C, 51.15; H, 8.55; N, 14.70; S, 16.9%.

A picrate formed in the usual manner melted at 154–155°C., yield 77.2%. Calc. for $C_{14}H_{19}N_5O_8S$: C, 40.27; H, 4.58; N, 16.7%. Found: C, 40.33; H, 4.88; N, 16.6%.

A sample (2.8 gm., 0.015 mole) of 5-diethylaminomethyloxazolidine-2-thione in 9 cc. of methanol was treated with hydriodic acid (2.05 cc., $d = 1.7$). On addition of dry ether (150 cc.) to this solution, an oil separated. This oil crystallized (m.p. 113–120°C.) on standing, yield 4.23 gm. (90.0%). Two crystallizations from ethanol raised the melting point of the hydroiodide salt to 124–126°C. Calc. for $C_8H_{17}IN_2OS$: C, 30.39; H, 5.42; N, 8.86%. Found: C, 30.60; H, 5.60; N, 9.0%.

5-Diethylaminomethyl-2-oxazolidone

1-Amino-3-diethylamino-2-propanol (18.31 gm., 0.125 mole) and diethyl carbonate (22 gm., 0.186 mole) were condensed in the presence of sodium methylate catalyst (0.10 gm.) by the method of Homeyer (5). After removal of the excess ethyl carbonate *in vacuo* under nitrogen, an oil was obtained, yield 19.09 gm. (88.5%). This oil crystallized (m.p. 40–43°C.) on standing and two crystallizations from ethanol raised the melting point to 51.5–53°C. Calc. for $C_8H_{16}N_2O_2$: C, 55.80; H, 9.37; N, 16.27%. Found: C, 56.10; H, 9.41; N, 15.9%.

A sample (1.0 gm., 0.0058 mole) of 5-diethylaminomethyl-2-oxazolidone was refluxed with methyl iodide (0.825 gm., 0.0058 mole) in absolute methanol for 30 min. This solution was cooled to room temperature and allowed to stand for 15 hr. Colorless crystals (m.p. 158–161°C.) were deposited from the solution, yield 1.235 gm. (67.7%). Two crystallizations from absolute ethanol raised the melting point to a constant value of 160.5–161.5°C. Calc. for $C_9H_{19}IN_2O_2$: C, 34.41; H, 6.09; I, 40.39; N, 8.92%. Found: C, 34.22; H, 5.94; I, 40.58; N, 9.04%.

Infrared Spectra

The infrared spectra were obtained with a Perkin-Elmer single beam spectrophotometer equipped with a sodium chloride prism. The samples were observed as mulls of the solid in Nujol.

ACKNOWLEDGMENT

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FRACTIONATION OF POLYSACCHARIDES[1]

By A. J. Erskine[2,3] and J. K. N. Jones[3]

ABSTRACT

A method for fractionation of water-soluble polysaccharide mixtures has been examined, and by its use three of the four materials studied have been separated into two or more polysaccharide components. No fractionation of the fourth material could be detected.

In the study of polysaccharides one of the first requirements is that the material be chemically homogeneous, i.e. that further fractionation of the polysaccharide yields products having the same specific rotations and the same ratio of monosaccharide building units. Most reports of such work include attempts to fractionate the material in question. However, little effort has been made to develop standard methods for this purpose such as are used in protein chemistry. The method to be described has proved reasonably satisfactory for three of the four water-soluble polysaccharides investigated. It is hoped that the procedure may prove to be generally applicable, and later experiments may show whether it can be used to fractionate water-insoluble, alkali-soluble polysaccharide mixtures.

Methods of fractionation of polymers now in use are based upon many properties. Electrophoresis is one way of testing the chemical homogeneity of polysaccharide materials, but it can only be used to separate micro-quantities, and the same is true of the ultracentrifuge. These methods are not at present of preparative value, although they may give information which can be used to interpret or correct results obtained by other means. Solvent partition has been widely used for separating mixtures of methylated or acetylated polysaccharides, but the unsubstituted materials are usually too insoluble in solvents other than water to permit use of these methods. Consequently, most attempts to fractionate polysaccharides make use of precipitation and inevitably suffer from the faults of coprecipitation, occlusion, etc., as most precipitates so obtained are voluminous and jelly-like. In these respects the present method offers little or no improvement, but the ease with which the neutral components of polysaccharide mixtures are isolated is a definite advance.

In most cases a solution of precipitant is added to an aqueous solution of the polysaccharide. Occasionally alcohol will effect a partial separation of the components of a mixture (e.g., 5).[4] Recently Jones (12) found that cetyl trimethylammonium bromide could be used to precipitate the acidic components from a mixture of polysaccharides. Bailey (3) used solutions of baryta or sodium hydroxide with moderate success. However, the majority of workers have employed solutions of copper salts to effect separation of polysaccharides.

[1]*Manuscript received February 17, 1956.*
Contribution from the Department of Chemistry, Queen's University, Kingston, Ont.
[2]*Holder of an N.R.C. Bursary 1953–54, and of N.R.C. Studentships 1954–56.*
[3]*Department of Chemistry, Queen's University, Kingston, Ont.*
[4]*The references cited are not the only cases in which a specific precipitant was used.*

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Fehling's solution is often used (6), possibly because it is a common reagent in the laboratory, while solutions of "cupri-ethylenediamine" (4), cupric chloride (1), cupric sulphate (9), and cupric acetate (7) have also been used. In most cases an excess of precipitant is added and the precipitate is removed by either filtration or centrifugation. The "copper complex" is then decomposed by an alcoholic solution of acid or a chelating agent, and the precipitate washed until free from inorganic ions. Frequently a further precipitate is obtained from the filtrate by addition of alcohol, and this sequence of operations is sometimes repeated as many as thirty times.

This paper describes attempts to fractionate mixtures of polysaccharides using cupric acetate solution and ethanol as precipitants, but with the important difference that no more of each is added at any one time than is necessary to initiate precipitation. In this manner it was shown that the mucilage from linseed (*Linum usitatissimum*) is a mixture of not less than three distinct polysaccharides. This success led to attempts to fractionate other common plant mucilages. No fractionation of the mucilage from the bark of slippery elm (*Ulmus fulva*) could be detected, but the seed mucilages from *Plantago ovata* and *P. arenaria*[5] were each shown to contain at least two polysaccharide components. The constants determined to assess whether a fractionation had been effected were (1) optical rotation, (2) equivalent weight, and (3) paper chromatographic examination of the sugars produced upon hydrolysis of the fractions. In each case it was found possible to obtain one fraction containing less than one per cent of uronic acid after refractionation (see experimental section). Although similar in composition these fractions differ in optical rotation and evidently vary with their source.

These results may be compared with those obtained by earlier workers. It has been reported (3) that linseed mucilage can be fractionated by means of baryta, and Easterby and Jones (7) determined the proportions of sugars present in two fractions which were obtained from this material, using cupric acetate and ethanol as precipitants. It is evident from the constants reported for their fractions that these workers effected only a partial separation of linseed mucilage into its components. The failure to fractionate slippery elm mucilage is in agreement with the results of Gill *et al.*, who found it to be homogeneous when methylated (8). Laidlaw and Percival (13) studied *Plantago ovata* mucilage and observed that varying conditions of preparation yielded products with different properties. This was in agreement with the work of Anderson and Fireman (2) on the seed mucilage of *Plantago psyllium* (believed to be synonymous with *P. ovata*). Laidlaw and Percival (13) obtained two products, with equivalent weights of 700 and 4000 respectively, but upon methylation both gave uronic acid free polysaccharides of similar but not identical composition. The present work confirms that a neutral polysaccharide is present in *P. ovata* mucilage, and does not preclude the isolation of a polyuronide from the acidic component by further fractionation. Several groups of workers have investigated *Plantago arenaria* mucilage without

[5]*More correctly known by the older name P. indica (private communication by D. S. Erskine).*

attempting its fractionation (10, 11, 14), and here also a neutral polysaccharide was obtained upon methylation of a uronic acid containing material (14). Our results confirm the presence of a neutral compound and, as in the case of *P. ovata*, admit the possibility of isolating a polyuronide from the acidic component by refractionation.

EXPERIMENTAL

General Procedure

As far as was possible all materials were prepared under the same conditions. The raw materials—seeds or finely shredded bark—were stirred with 10 times their weight of water for six hours at room temperature. The mucilaginous solution was separated by pouring it through a Buchner funnel (without paper), followed by straining it through muslin. The polysaccharide was precipitated by pouring the solution into two volumes of absolute ethanol containing concentrated hydrochloric acid (10 ml./liter of ethanol) and enough ice to keep the reaction mixture at or below room temperature. The precipitated material was lifted out, washed with absolute ethanol to remove acid, and redissolved in about 15–20 times its weight of water. The aqueous solution was centrifuged to remove insoluble material, and cupric acetate solution (7%, w/v in water) was added until precipitation occurred. The precipitate was removed by centrifugation, and cupric acetate solution was added until a maximum concentration of 0.40% of cupric acetate was reached. If no precipitate had formed, ethanol was added portionwise and each precipitate so formed was removed before further precipitant was added. In all cases the copper complex was decomposed by twice macerating the precipitate in a Waring Blendor with absolute ethanol containing 5% v/v of concentrated hydrochloric acid for one minute or less. The resulting polysaccharides were washed with absolute ethanol until the washings gave a negative test for chloride, and were dried under vacuum to constant weight before examination.

For analysis a 50 mgm. (approx.) sample was weighed out and dissolved in water (5 ml.). The optical rotation of this solution was determined, if possible, and duplicate 1 ml. samples were titrated with $N/10$ sodium hydroxide solution, using an Agla micrometer syringe. A sample of the solution was hydrolyzed with N sulphuric acid at 90–95° for 24 hr., the acid was neutralized ($BaCO_3$ or $Ba(OH)_2$), and the resulting precipitate removed. The solution was concentrated and the sirup examined on paper chromatograms in the two solvent mixtures—ethyl acetate/acetic acid/formic acid/water, 18/3/1/4, and butanol/pyridine/water, 10/3/3. Sugars were identified by their rates of movement relative to a standard mixture of sugars.

The linseeds were obtained from W. Peters and Sons Seed Co., Kingston, Ont., while the slippery elm bark is a product of S. B. Penick & Co., Botanical Drugs, New York, N.Y. The *Plantago ovata* and *P. arenaria* seeds were samples of "Psyllium seed blond" and "Psyllium seed black" respectively, obtained from S. B. Penick & Co., and identified by D. S. Erskine, Department of Geography, University of Toronto, Toronto, Ont.

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Linseed Mucilage

The polysaccharide mixture was prepared exactly as described above, in 4% yield. Samples prepared from seeds obtained at different times showed the same properties. The results from a typical fractionation are given in Table I. Fractions with similar properties were combined and refractionated,

TABLE I

FRACTIONATION OF LINSEED MUCILAGE

Fraction	% $CuAc_2$ for pptn.	% EtOH for pptn.	Fraction of starting material	$[\alpha]_D$	$c(H_2O)$	Equiv. wt.
I	0.18	0	21.0	+57°±10°	0.75*	—
II	0.41	16	53.2	+ 7°± 3°	1.11	646
III	0.25	49	9.0	−38°± 3°	1.08	2560
IV	0.18	64	10.8	−50°± 3°	1.04	24900

**In 0.03 N NaOH solution.*

giving, eventually, fractions with the properties shown in Table II. Further fractionation is being carried out on fractions *A* and *B* (Table II) in the hope

TABLE II

PROPERTIES OF POLYSACCHARIDES ISOLATED FROM LINSEED MUCILAGE

Fraction	% of total	$[\alpha]_D$	Equiv. wt.	Products on hydrolysis						
				Rham.	Fuc.	Xyl.	Ara.	Glu.	Gal.	G.A.
A	15	+95°±5°	390±20	+++	+	+++	+		+	+++
B	65	+10°±5°	550±30	+	+	Trace			+++	++
C	20	−49°±2°	—			+++	++	+	+	

Rham. = Rhamnose, Fuc. = Fucose, Xyl. = Xylose, Ara. = Arabinose, Glu. = Glucose, Gal. = Galactose, G.A. = Galacturonic acid.

of obtaining a pentose-free polysaccharide from the latter. No further separation of fraction *C* could be obtained and structural studies on this material are in progress.

Slippery Elm Mucilage

The slippery elm bark was shredded into fragments not larger than approx. 1/4 in. by 1/4 in. by 1/32 in., and extracted with benzene–ethanol solution (2/1, v/v) to remove oils and resinous materials. The preparation then followed the general procedure outlined above, and the polysaccharide was obtained as a crumbly light-brown solid in 8% yield. This material was very sparingly soluble in cold water, and almost completely insoluble in dilute alkali solutions, so fractionation was rather unsatisfactory. It was not possible to determine optical rotations of the fractions, and titration of their heterogeneous dispersions was accompanied by a high degree of error. Equivalent weights for the three fractions obtained in one operation varied from 520 to 580 which was

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within the experimental error under those conditions. All fractions gave the same products upon hydrolysis, namely: rhamnose, 3-*O*-methyl galactose, galactose, and galacturonic acid, in approximately equal proportions, with a smaller amount of xylose.

Plantago ovata Mucilage

The seeds of *Plantago ovata* gave an exceedingly viscous solution with water. Even when dispersed in 25 times their weight of water the suspension could not be filtered upon a Buchner funnel in the usual manner, but when it was left overnight the seeds and a dense gel settled out and the clear solution on top could be decanted. Similarly, centrifugation gave a clear solution and a gel, which were fractionated separately. Upon refractionation the components listed in Table III were obtained.

TABLE III

PROPERTIES OF FRACTIONS OBTAINED FROM *Plantago ovata* MUCILAGE

Fraction	% of total	$[\alpha]_D$	$c(H_2O)$	Equiv. wt.	Products on hydrolysis					
					Rham.	4mGl.A.	Xyl.	Ara.	Gal.	G.A.
(*S*)olution 1	9	+ 23°	1.14	710	++	Trace	+++	++	+	++
*S*2	12	− 40°	1.16	1300	+	Trace	+++	+	+	+
*S*3	15	−108°	0.92	34000			+++	+	Trace	
(*G*)el 1	54	—	—	2400	+	+	+++	++	+	+
*G*2	10	− 68°	0.58	1900						

Rham., Xyl., Ara., Gal., G.A., as in Table II; 4mGl.A. = 4-O-methyl glucuronic acid.

From these properties it is thought likely that refractionation of *S*2 and *G*2 would yield largely the product present in *S*3, which is qualitatively similar to that isolated after methylation by Laidlaw *et al.* (13). Fraction *S*1 is presumably the same as their polysaccharide *P*1, to which it corresponds closely in equivalent weight and composition. Their work suggests that refractionation of our product might separate a component, containing all of the rhamnose and galacturonic acid, with a still lower equivalent weight. Fraction *G*1 contains some impurity that renders it relatively insoluble in water, but the concentration of an acidic sugar assumed from its rate to be 4-*O*-methyl glucuronic acid (not previously detected in this material) in this fraction suggests that yet a third polysaccharide may be involved.

Plantago arenaria Mucilage

The polysaccharide mixture was prepared and fractionated as described in the general procedure. As before, the fractions initially precipitated gave more opaque solutions than those isolated later, but most unexpectedly it was found that the acidic fraction was the last to be precipitated. A relatively small amount of an acidic polysaccharide was obtained from the last fraction, and this is in agreement with earlier results (10, 11, 14). As in the case of *Plantago ovata* previous workers found no uronic acid or rhamnose in their methylated products, so here again the isolation of a polyuronide upon refractionation may be possible.

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TABLE IV

PROPERTIES OF FRACTIONS OBTAINED FROM *Plantago arenaria* MUCILAGE

Fraction	$[\alpha]_D$	Equiv. wt.	Products on hydrolysis				
			Rham.	Xyl.	Ara.	Gal.	G.A.
A 1*a*	—	25000		+++	++	+	
A 1*b*	—	12000		+++	++	+	
A 1*c*	−54°	19000		++	+	+	
A 2	−42°	3500					
B 1*a*	−55°	25000		++	++	+	
B 1*b*	—	7100		+++	++	+	
B 2	+45°	670	++	++	++	+	++

Abbreviations as before.

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PREPARATION OF GUANIDINE FROM UREA, SULPHUR DIOXIDE, AND AMMONIA UNDER PRESSURE[1]

By Jean L. Boivin

ABSTRACT

It has been found that guanidine can be prepared in good yield from urea, sulphur dioxide, and ammonia under pressure over a wide range of conditions. A study of the effect of concentration, temperature, time, and pressure has been made. A part of the sulphur dioxide introduced into the reaction vessel can be recovered as elemental sulphur. Guanidine nitrate is easily prepared by treating the reaction product with dilute nitric acid. The mechanism of this synthesis has been found to proceed through the formation of ammonium sulphamate from sulphur dioxide and ammonia. Guanidine was present as the sulphamate when synthesized at low temperatures and as the sulphate at high temperatures.

Ammonia and sulphur trioxide react under suitable conditions to yield ammonium sulphamate (Eq. 1) with some triammonium imidosulphonate (Eq. 2) and sulphamide (Eq. 3).

$$SO_3 + 2NH_3 \rightarrow H_2NSO_3NH_4 \quad [1]$$

$$2SO_3 + 3NH_3 \rightarrow NH_4N(SO_3NH_4)_2 \quad [2]$$

$$SO_3 + 2NH_3 \rightarrow NH_2SO_2NH_2 + H_2O \quad [3]$$

The complex product, obtained from ammonia and sulphur trioxide, is known to yield guanidine sulphamate when heated under pressure with urea and ammonia (3). For convenience of description, only the ammonium sulphamate will be considered, since analogous reactions can be inferred for the other two compounds.

The reaction of sulphur dioxide and ammonia, although not clearly understood, is believed to be similar to that with sulphur trioxide and ammonia.

$$SO_2 + 2NH_3 \rightarrow H_2NSO_2NH_4 \quad [4]$$

$$2SO_2 + 3NH_3 \rightarrow H_4N{-}N(SO_2NH_4)_2 \quad [5]$$

$$SO_2 + 2NH_3 \rightarrow H_2NSONH_2 + H_2O \quad [6]$$

In the actual preparation of this complex, an excess of ammonia is reacted with sulphur dioxide. The reaction is exothermic. A nearly white product is obtained, but there is always present a red substance which is reported to be triammonium imidosulphinate (1).

When urea, sulphur dioxide, and ammonia are reacted in the molar ratio of 1:3:7 under suitable conditions, urea is converted into guanidine in yields exceeding 80%. It has been found, however, that in all cases one third of the sulphur dioxide taken is recovered in the form of elemental sulphur, which is easily filtered. The filtrate, after evaporation to small volume and treatment with excess of dilute nitric acid, yields guanidine nitrate while some sulphur dioxide is evolved.

[1]*Manuscript received March 1, 1956.*
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In view of the presence of sulphur in the reaction mixture, it appears that an oxidoreduction process takes place, possibly according to the over-all equation

$$2H_2N{-}\overset{\uparrow}{\underset{O}{S}}{-}ONH_4 + \overset{\uparrow}{\underset{O}{S}}{=}O \rightarrow S + 2(NH_4)_2SO_4. \qquad [7]$$

However, an alternative mechanism could be considered for the formation of sulphur. The amount of sulphur found in the present synthesis of guanidine was nearly constant at one mole when three moles of sulphur dioxide was used; this equation accounts for formation of sulphur and sulphate.

A preliminary investigation of the factors involved in this synthesis of guanidine from urea has been made. In all cases, the ammonia – sulphur dioxide complex was formed below −30° C. in the glass liner of an ordinary Parr bomb, and urea was added to the mixture. After the mixture was heated to the desired temperature over a period of time under ammonia pressure, the mass, which was still liquid at 150° C., was boiled in water. Sulphur was removed by filtration and the filtrate was analyzed for guanidine and melamine contents.

TABLE I

EFFECT OF TEMPERATURE

Urea: 0.1 mole; sulphur dioxide: 0.3 mole; ammonia: 0.7 mole; pressure: 200 p.s.i.g.; heating time: 1 hr.

Temp., °C.	Yield based on urea guanidine, %	Melamine, %
215	1	0
235	64	0
245	80	0
265	81	0
275	76	6.1
285	51	17
295	46	35
305	42	44

Effect of Temperature

It can be seen that 80% yield of guanidine (Table I) can be obtained between 245° C. and 265° C. under the present conditions without the production of melamine which is due to the decomposition of the guanidine formed. The guanidine formation increased with temperature, reached a maximum value, and then decreased when melamine appeared in the mixture.

TABLE II

EFFECT OF CONCENTRATION OF UREA

Sulphur dioxide: 0.3 mole; ammonia: 0.7 mole; temp.: 275°C.; pressure: 200 p.s.i.g.; heating time: 1 hr.

Urea, mole	Yield based on urea guanidine, %	Melamine, %
0.05	60	0
0.10	74	0
0.15	56	0
0.20	43	10.3
0.30	26	8.1

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Effect of Concentration of Urea

The optimum amount of urea seemed to be one tenth of a mole under the actual conditions (Table II). At high concentrations of urea, a considerable amount of cyanuric acid was found in addition to unreacted urea.

Effect of Time

The effect of the period of heating has been studied at 255°, 275°, and 305° C. The reaction time given is measured from the attainment of the stated temperature.

TABLE III

EFFECT OF TIME

Urea: 0.1 mole; sulphur dioxide: 0.3 mole; pressure: 200 p.s.i.g.; ammonia: 0.7 mole

Temp., °C.	Time, min.	Yield based on urea guanidine, %
255	30	73
255	60	81
255	90	72
275	30	82
275	60	74
275	90	70
305	5	51
305	10	57
305	15	55
305	60	42

It can be noted that a higher temperature decreases the heating time (Table III). The reaction seems to proceed twice as fast when temperature is increased by 20° C. However, at 305° C. optimum yield is low and it seems that this reaction could not be effected with good yields at high temperature with the equipment used.

Effect of Pressure

From the point of view of equipment design and operation, pressure requirements frequently have a major influence on cost and safety. In the reaction, the effect of pressure is negligible from 200 to 3000 p.s.i.g., as can be seen in Table IV. Even under a pressure of 75 p.s.i.g., a 74% yield could be obtained.

TABLE IV

EFFECT OF PRESSURE

Urea: 0.1 mole; sulphur dioxide: 0.3 mole; temp.: 275°C.; heating time: 30 min.

NH_3, mole	Pressure, p.s.i.g.	Guanidine, %
2.0	3000*	83
2.0	1000*	82
0.7	200*	82
0.7	75*	74
0.7	0	46

**Vented to this pressure, after attaining prescribed temperature.*

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Good yields may be obtained over a wide range of conditions. Pressures as low as 75 p.s.i.g. are capable of giving 75% yield. This would simplify the construction of a reaction vessel. An important feature is ready isolation of guanidine in the form of its nitrate. In view of the good yields obtained and the cheap starting materials used, special attention was devoted to elucidate the mechanism of the synthesis.

A review of the literature dealing with ammonium amidosulphinate was not too conclusive for the elucidation of the mechanism. Divers and Ogawa (1) found that ammonium amidosulphinate when heated yields ammonia and ammonium imidosulphinate, a reaction similar to the formation of ammonium imidosulphonate from ammonium sulphamate. They also explain that the reaction between ammonia and sulphur dioxide yields mainly ammonium imidosulphinate, the latter decomposing on heating into volatile matter, sulphur, ammonium sulphate, and ammonium imidosulphinate. In spite of the numerous products isolated from the decomposition of the ammonia – sulphur dioxide complexes, the reaction under ammonia pressure is less intricate because of the recovery of sulphur which has always been made in 33% yield based on sulphur dioxide used. Guanidine was produced in high yields from urea under various conditions of temperature and pressure.

In the following discussion of the explanation of this reaction mechanism, experiments have been made as quantitative as possible considering the difficulties encountered when working with gaseous products and heating them in a bomb at high temperatures.

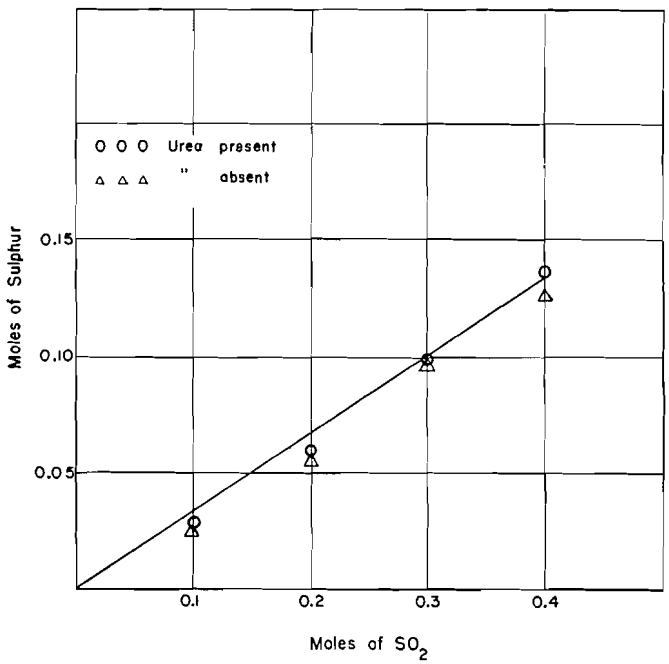

FIG. 1. Formation of sulphur.

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Sulphur Formation

By heating together a mixture of urea, sulphur dioxide, and ammonia at 275° C. for half an hour, the yield of guanidine from urea was nearly constant at 80%, when the molar ratio of urea: sulphur dioxide: ammonia was 1:3:9. The variation of the amount of sulphur dioxide used resulted in a variation in the yield of guanidine from urea (Table V). It should also be noted that the formation of sulphur increased with the amount of sulphur dioxide added to the reaction mixture, the yield being nearly constant at 33%. If a graph is made by plotting the molar amounts of sulphur produced against the molar quantities of sulphur dioxide used, a straight line is obtained (Fig. 1).

To prove that urea had no participation in the reaction involving the production of sulphur, the same series of experiments were effected in its absence (Table VI). It was found that sulphur was produced in nearly the same yield as when urea was present.

It was also thought that the formation of sulphur might be an equilibrium reaction. An experiment was made (No. 84, Table V) in which sulphur was added to the reaction mixture. The total amount of sulphur was nearly equal to the sulphur added and the sulphur usually produced from sulphur dioxide.

TABLE V

SULPHUR BALANCE IN THE FUSION OF UREA, SULPHUR DIOXIDE, AND AMMONIA

Run No.	SO_2, mole	Urea, mole	NH_3, mole	Sulphur produced, mole	$BaSO_4$(O), mole *A*	$BaSO_4$(HCl) mole *B*	*A* − *B*	Guanidine, mole	Pressure, p.s.i.g.	Sulphur balance, mole
83	0.1	0.1	0.9	0.0293	0.080	0.058	0.022	0.042	2400	0.109
82	0.2	0.1	0.9	0.061	0.142	0.076	0.066	0.069	1850	0.203
81	0.3	0.1	0.9	0.098	0.212	0.128	0.084	0.083	1400	0.310
85	0.4	0.1	0.9	0.132	0.260	0.118	0.142	0.073	800	0.392
84	0.3–0.1255*	0.1	0.9	0.196	0.209	0.133	0.076	0.076	200 (vented)	0.405

**Elemental sulphur added.*

NOTE: *The bomb was heated at 275°C. for 30 min. in all the above experiments.*

Thus the addition of sulphur does not appreciably depress its formation; therefore, in the actual synthesis the formation of sulphur does not result from an equilibrium reaction.

Sulphate Formation

Since sulphates were present in the reaction mixture, experiments were carried out to determine the effect of urea on the ammonia – sulphur dioxide complex. After the ingredients had been heated in the same way as mentioned in Tables I and II, the reaction products were dissolved in water and the solution filtered free of sulphur. The filtrate was analyzed for sulphate ion content. It was to be expected that the reaction mixture might contain reducing sulphur compounds like sulphites and thiosulphates, and that a determination of the actual sulphate would be of value. The method involved the cold treatment of a portion of this solution with barium chloride in hydrochloric acid. Results are given in Tables V and VI and shown graphically in Figs. 2 and 3. It can be seen that the molar quantities of sulphate produced from sulphur dioxide are nearly linear in the absence of urea.

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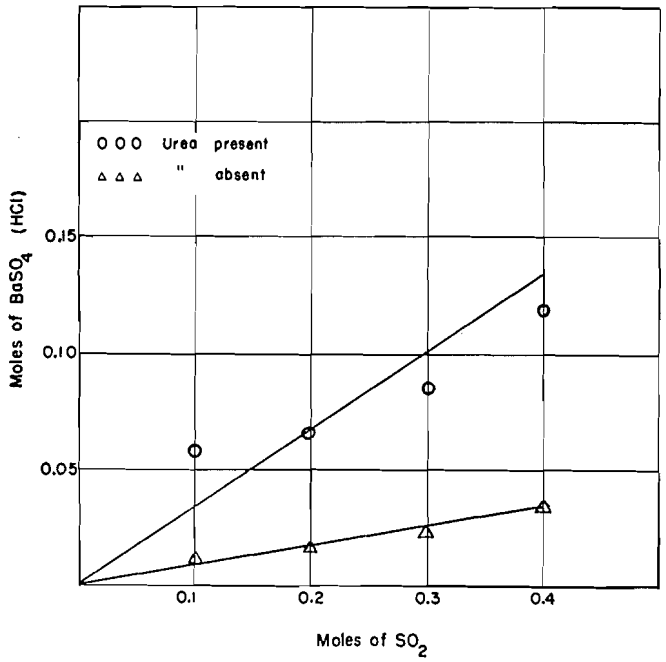

FIG. 2. Formation of barium sulphate (HCl).

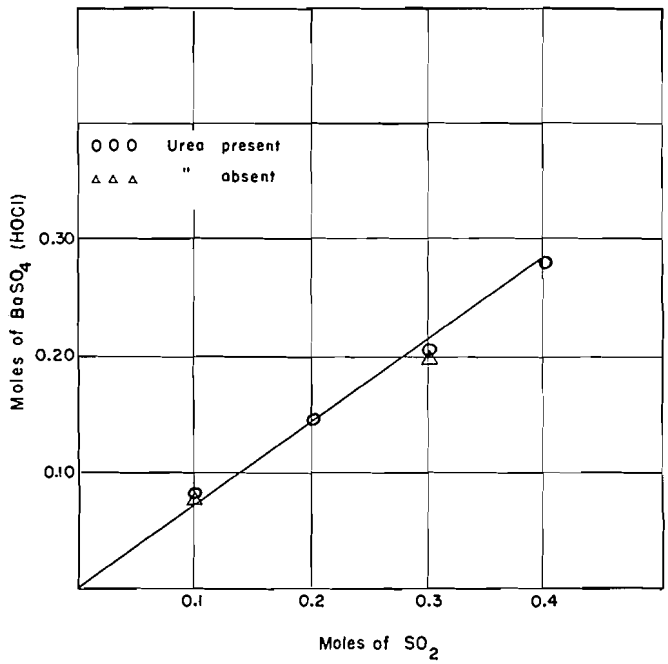

FIG. 3. Formation of barium sulphate (HOCl).

However, what is important in these experiments is the marked increase of sulphate formed when urea is present, i.e. when guanidine is produced.

TABLE VI

SULPHUR BALANCE IN THE REACTION OF SULPHUR DIOXIDE AND AMMONIA

Batch No.	SO_2, mole	NH_3, mole	Pressure, p.s.i.g.	NH_3 recovered in moles	NH_3 used	Sulphur produced in moles	$BaSO_4(O)$, mole A	$BaSO_4(HCl)$, mole B	$A-B$	Sulphur balance, mole
86	0.1	0.9	2800	0.62	0.28	0.025	0.072	0.013	0.059	0.097
87	0.2	0.9	2200	0.55	0.35	0.057	0.143	0.019	0.124	0.201
88	0.3	0.9	1700	0.35	0.55	0.102	0.200	0.024	0.176	0.302
89	0.4	0.9	950	0.25	0.65	0.123	0.278	0.037	0.241	0.401

NOTE: *The bomb was heated at 275°C. for 30 min.*

The determination of total sulphur-containing compounds in the form of sulphate was thought to be of interest in view of obtaining a good sulphur balance. The estimation was made by oxidizing the reducing sulphur compounds present in the solution to sulphate by means of sodium hypochlorite. Fig. 3 shows that the sulphate content, expressed in moles of barium sulphate, increases linearly with increasing amounts of sulphur dioxide, with or without urea, the molar values of sulphate being the same.

Ammonium Sulphamate

If subtraction is made between the molar value of sulphate present after the oxidation of the solution ($BaSO_4(O)$) and the molar quantity of true sulphate ($BaSO_4(HCl)$) when urea was present, values are obtained which are nearly proportional to the quantities of sulphur dioxide present up to 3 moles per mole of urea (Fig. 4).

$$BaSO_4(O) - BaSO_4(HCl) = C$$

This value "*C*" was found to be equal to the molar quantities of guanidine produced from urea. For instance, in Table V, run No. 81 shows the molar quantity of sulphates formed. This value "*C*" is: $0.212-0.128 = 0.084$. Hence this value "*C*" is related to the formation of guanidine.

Results also show that the amount of oxidized sulphur-containing compounds as barium sulphate (Tables V and VI), either in the presence of urea or in its absence, is proportional to the amount of sulphur dioxide present in the reaction mixture (Fig. 3).

Moreover, if summation of molar quantities of elemental sulphur and total sulphates formed is made, a good sulphur balance is obtained, as for instance in run No. 82 of Table V and in run No. 87 of Table VI.

From the data of Tables V and VI, proportionality of production of sulphur has been observed in respect to sulphur dioxide in the presence or absence of urea; the same fact has been observed of the actual sulphate present when urea was added to the ammonia – sulphur dioxide complex. In its absence, this value "*C*" was proportional to the amount of sulphur dioxide used (Fig. 4).

Therefore, there is a relationship between the formation of sulphates, sulphur, and guanidine. It was thought that the ammonium sulphamate

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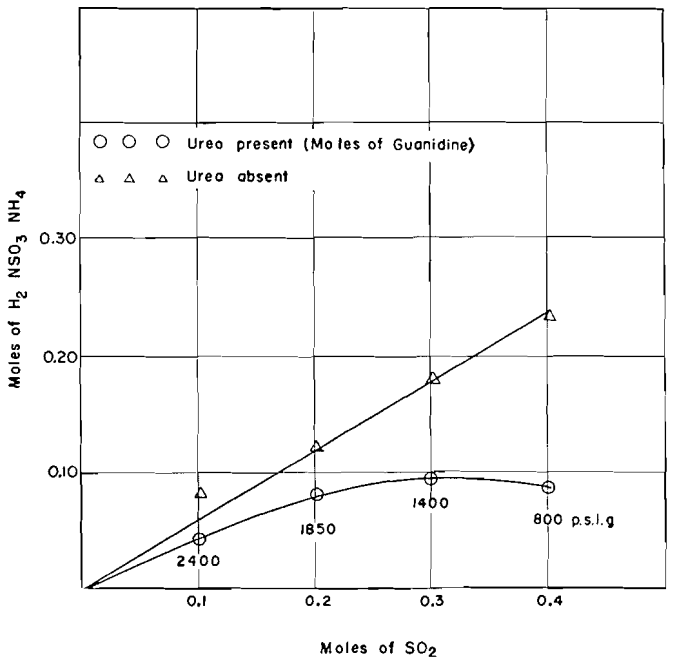

FIG. 4. Formation of ammonium sulphamate.

isolated in low yields by Divers and Ogawa (1) when they heated the ammonia – sulphur dioxide complex was probably the predominant compound under the actual conditions where excess of ammonia is used. If so, guanidine should be present as the sulphamate or sulphate. Guanidine sulphamate is soluble in liquid ammonia and slightly soluble in ethanol whereas guanidine sulphate is insoluble in both solvents. By extraction of the reaction products with liquid ammonia, guanidine sulphamate was identified and isolated in good yields.

After the isolation of guanidine sulphamate, there was evidence that the actual synthesis was a sulphamate synthesis of guanidine from urea. Therefore, the heating of sulphur dioxide with excess of ammonia under pressure should yield ammonium sulphamate and sulphur as the main products, ammonium sulphate being present in quantities equivalent to the guanidine formed.

When sulphur dioxide and ammonia were heated at 275° C. for half an hour (Table VI), the reaction mixture contained molten products at 125° C. The melt was extracted with liquid ammonia and the solution filtered. After evaporation, a crystalline product was obtained which was found to be ammonium sulphamate. The yields of ammonium sulphamate were excellent.

Mechanism of the Synthesis

The mechanism of the formation of ammonium sulphamate can be thus explained. At low temperature an ammonia – sulphur dioxide complex will be

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formed consisting of ammonium amidosulphinate (Eq. 8) and ammonium imidosulphinate (Eq. 9).

$$SO_2 + 2NH_3 \underset{100\text{–}150°C.}{\overset{-10°C.}{\rightleftharpoons}} H_2N—SO_2NH_4 \quad [8]$$

$$2SO_2 + 3NH_3 \underset{100\text{–}150°C.}{\overset{-10°C.}{\rightleftharpoons}} NH\begin{matrix}\diagup SO_2NH_4 \\ \diagdown SO_2NH_4\end{matrix} \quad [9]$$

But by heating these two compounds in excess of ammonia, they should dissociate incompletely yielding ammonia and sulphur dioxide.

It is known that sulphur dioxide activated by light (2) dissociates into colloidal sulphur and sulphur trioxide according to the following equilibrium reaction:

$$3SO_2 \rightleftharpoons S + 2SO_3. \quad [10]$$

If so, the formation of ammonium sulphamate will be readily explained from sulphur dioxide and ammonia:

$$SO_3 + 2NH_3 \longrightarrow H_2NSO_3NH_4. \quad [11]$$

In this synthesis the formation of sulphur has been found to take place at about 150° C. It may be deduced that, owing to thermal activation of the sulphur dioxide molecule, it should dissociate in the presence of ammonia, as above, yielding sulphur and sulphur trioxide. Thus the over-all reaction of sulphur dioxide and ammonia will be represented by the following equation:

$$3SO_2 + 4NH_3 \longrightarrow S + 2NH_2SO_3NH_4. \quad [12]$$

The isolation of guanidine sulphamate from a mixture of urea, sulphur dioxide, and ammonia in molar ratio 1:3:9 is not surprising. From experiments described earlier it has been found that guanidine is produced at a temperature

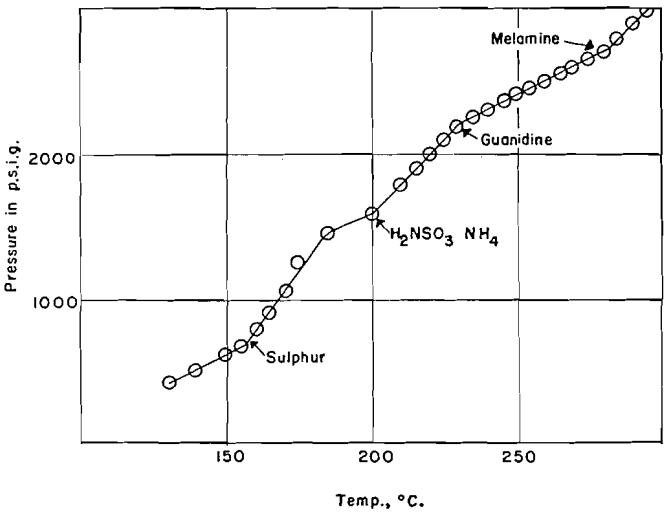

FIG. 5. Pressure–temperature curve.

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of about 220° C. Sulphur is formed at a temperature as low as 160° C., therefore sulphamate should be produced. This is shown graphically in Fig. 5 where pressure is plotted against the temperature.

The synthesis of guanidine from urea, sulphur dioxide, and ammonia under pressure proceeds in two main steps. First ammonium sulphamate is produced from sulphur dioxide and ammonia:

$$3SO_2 + 4NH_3 \longrightarrow 2NH_2SO_3NH_4 + S \qquad [13]$$

then urea reacts with ammonium sulphamate yielding guanidine sulphamate:

$$\begin{matrix} NH_2 \\ | \\ C{=}O \\ | \\ NH_2 \end{matrix} + 2NH_2SO_3NH_4 \longrightarrow \begin{matrix} NH_2 \\ | \\ C{=}NH \\ | \\ NH_2.NH_2SO_3H \end{matrix} + (NH_4)_2SO_4 \qquad [14]$$

$$3SO_2 + 4NH_3 + \begin{matrix} NH_2 \\ | \\ C{=}O \\ | \\ NH_2 \end{matrix} \longrightarrow \begin{matrix} NH_2 \\ | \\ C{=}NH \\ | \\ NH_2.NH_2SO_3H \end{matrix} + (NH_4)_2SO_4 + S \qquad [15]$$

Guanidine Sulphamate and Sulphate

The formation of guanidine increased, as was expected, with the amount of sulphur dioxide used (Fig. 4), but decreased owing to dilution with excess of sulphur dioxide (0.4 mole vs. 0.1 mole urea). When a mixture of urea, sulphur dioxide, and ammonia (molar ratio 1:3:9) was heated at 275° C. for an hour at a pressure of 200 p.s.i.g., guanidine was present mainly as the sulphamate. Alternatively, the same reaction mixture heated at 300° C. for two to five minutes and cooled immediately yielded mainly guanidine sulphate. Guanidine sulphamate is soluble in liquid ammonia whereas guanidine sulphate is very insoluble. Therefore a means of separating the two salts of guanidine is suggested.

When urea, sulphur dioxide, and ammonia were used in the molar ratio 2:3:7, guanidine sulphate was produced in 43.6% yield, traces of guanidine sulphamate being formed. Melamine was obtained also in good yield owing to the instability of guanidine sulphate under the conditions employed. At a lower temperature of synthesis, for instance at 275° C., less melamine is produced, but the yield of guanidine sulphate is decreased. The reactions involved when two moles of urea are used are as follows:

$$2\begin{matrix} NH_2 \\ | \\ C{=}O \\ | \\ NH_2 \end{matrix} + 3SO_2 + 4NH_3 \longrightarrow \left(\begin{matrix} NH_2 \\ | \\ C{=}NH \\ | \\ NH_2 \end{matrix} \right)_2 .H_2SO_4 + S + (NH_4)_2SO_4$$

Guanidine Nitrate

A series of runs were made at 275° C. from urea, sulphur dioxide, and ammonia (molar ratio 1:3:7) under which conditions 80% yield of guanidine or better was obtained. The reaction products were dissolved in boiling water, sulphur was filtered, and the filtrate treated with various quantities of nitric acid. Table VII shows the proportions and the amounts of guanidine nitrate

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TABLE VII

GUANIDINE NITRATE

Run[1] No.	HNO_3 (70%), gm.	Molar ratio, urea: HNO_3	Crude G.N.[2]		Recrystallized G.N.[3] from 20 ml. of water		% Yield of G.N. from urea
			gm.	m.p., °C.	gm.	m.p., °C.	
1	9.0	1:1	9.5	190–195	8.4	204–206	69
2	10.8	1:1.2	10.0	192–196	8.9	205–207	73
3	12.6	1:1.4	10.0	190–195	8.8	204–206	72
4	14.4	1:1.6	8.6	196–199	7.6	204–206	62
5	16.2	1:1.8	8.2	195–198	7.2	205–207	59

[1]*All runs were prepared by heating at 275°C. for half an hour at 200 p.s.i.g., urea:SO_2:NH_3 molar ratio being 1:3:9.*

[2]*Crystallization at 0°C. from 50 ml. of solution. G.N. = guanidine nitrate.*

[3]*Recrystallization at 0°C. from 20 ml. of water.*

isolated. The yields are very good if correction is made for solubility. It should be noted that a maximum yield of guanidine nitrate is obtained when the guanidine – nitric acid ratio is 1 : 1.35. Thus a yield of guanidine nitrate of 73% based on urea is obtained.

Conclusion

The synthesis of guanidine from urea, using sulphur dioxide and ammonia as dehydrating agent, is promising in that the starting materials are cheap and easily accessible. The ease of handling of sulphur dioxide and the large amount of this chemical distributed as sulphur or pyrites could render this synthesis applicable to continuous production of guanidine. This can be achieved by feeding an ammonia solution of urea and sulphur dioxide in a suitable reactor maintained at the desired temperature. The reaction products are molten at a temperature as low as 120° C.

EXPERIMENTAL

General Procedure

A 100 ml. autoclave was charged with urea, sulphur dioxide frozen in liquid air, and liquid ammonia. The bomb was heated at the desired temperature for a period of time. After the bomb was cooled, the contents of the glass liner was dissolved in water, sulphur was filtered off, and the clear solution used for analytical work.

Estimation of Sulphur

The crude sulphur obtained by filtration was dissolved in carbon disulphide and the solution evaporated in a weighed dish. Sulphur is reported in moles (Tables V and VI).

Estimation of Sulphates

(*a*) A 10 ml. aliquot portion of the solution made up to 500 ml. was diluted with 200 ml. of water and treated at room temperature with 50 ml. of 10% $BaCl_2$ solution in 2% hydrochloric acid. $BaSO_4$(HCl) is reported in moles (Tables V and VI).

(*b*) A 10 ml. aliquot portion was diluted with 100 ml. of water; 10 ml. of sodium hypochlorite (5% available chlorine) was added and the solution

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boiled. Hydrochloric acid was added until pH of 1–2 and then 50 ml. of 10% barium chloride added at the boiling point. The precipitate was filtered and weighed. $BaSO_4(O)$ is reported in moles (Tables V and VI).

Isolation of Guanidine Sulphamate

A mixture of urea (6.0 gm., 0.1 mole), sulphur dioxide (19.2 gm., 0.3 mole), and ammonia (15.3 gm., 0.9 mole) was heated at 275° C. for half an hour. The bomb was vented to 200 p.s.i.g. The contents of the glass liner was dissolved in water and sulphur was filtered off. The filtrate, after evaporation to dryness under reduced pressure, was treated with liquid ammonia (200 ml.) and the mixture filtered free of insoluble sulphates. The residue was washed well with ammonia. Analysis of the residue insoluble in liquid ammonia showed only traces of guanidine, presumably the sulphate. The liquid ammonia solution was allowed to evaporate and a residue was left which melted at 80–100° C. This material was recrystallized from alcohol and melted at 127° C. Further crystallizations raised the melting point to 128.5° C. A mixed melting point determination with guanidine sulphamate was not depressed.

Guanidine Sulphate

A similar batch was made by heating continuously to 300° C. and allowing the bomb to cool to 275° C. At this temperature the bomb was cooled with hot water and finally cold water. By working up the reaction products as above, it was found that the material insoluble in liquid ammonia contained 1.96 gm. of guanidine as sulphate and the liquid ammonia soluble material, 0.190 gm. of guanidine as sulphamate, thus giving a ratio of guanidine sulphamate to guanidine sulphate of 1: 10.

When the amount of urea was doubled leaving the quantities of other ingredients the same as above, all the guanidine was present as sulphate. A 43.6% yield of guanidine based on urea was obtained. The other part of urea was transformed into melamine.

Guanidine Nitrate

A series of batches from urea, sulphur dioxide, and ammonia (molar ratio 1: 3: 9) was prepared by heating at 275° C. for half an hour. The reaction products were dissolved in water and the sulphur was removed by filtration. The filtrate was treated with a known amount of 70% nitric acid (Table IV) and the solution evaporated on the hot plate to a volume of 50 ml. The solution was cooled to 0° C. and allowed to stand at this temperature for 10 min. The solid was filtered and washed once with water at 0° C. The melting point of guanidine nitrate was taken. The guanidine nitrate obtained was usually contaminated with urea nitrate. A recrystallization from 20 ml. of water gave a guanidine nitrate melting above 200° C. In Table VII it is seen that the optimum ratio of HNO_3 to guanidine is 1.35 to 1.

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NOTES

PALLADIUM AND SUBSTITUTED QUINOLINES

By D. E. Ryan

The structures suggested for the compound precipitated from palladous chloride solutions by 6-nitroquinoline have been based on the composition $Pd(C_9H_6NNO_2)_2$ (1, 2). It was reported recently, however, that chloride was present in the precipitated complex; analysis showed that an addition compound, $Pd(C_9H_6NNO_2)_2Cl_2$, was the product of the reaction between 6-nitroquinoline and palladous chloride (3). In the study of substituted quinolines as organic precipitants qualitative tests on their reaction with palladous chloride solutions were carried out and the results are of interest.

Ten milliliter samples of palladous chloride solution, containing approximately 1 mgm. Pd per ml., were diluted to 100 ml. with distilled water and the samples (pH 3) placed on the steam bath. A small amount of the quinoline being investigated was added and the samples allowed to digest for half an hour. Yellow precipitates were obtained with the following 15 compounds:

quinoline	6-methoxyquinoline	2-chloroquinoline
6-nitroquinoline	6-phenylquinoline	4-methylquinoline
6-methylquinoline	8-nitroquinoline	8-nitro-4-methylquinoline
6-bromoquinoline	8-methylquinoline	8-chloro-4-methylquinoline
6-chloroquinoline	8-chloroquinoline	benzo(f)quinoline

1,2,3,4-Tetrahydroquinoline reduced palladium II to the metal.

The results confirm that the nitro group is unimportant in the reaction of 6-nitroquinoline with palladous chloride solutions. Substitution for the nitro group, and the position of substituents on the quinoline nucleus, do not affect markedly the ability of the compound to replace chloride in $PdCl_4''$ to precipitate $(quinoline)_2PdCl_2$; such complexes can be extracted by organic solvents. Similar reactions were observed on adding the compounds to $PtCl_4''$ solutions. The failure to obtain precipitates from palladous chloride solutions containing excess cyanide or thiocyanate suggests that the quinolines are unable to displace ions from strong complexes such as $Pd(CN)_4''$.

The results emphasize that substituted quinolines react to form molecular rather than ionic complexes with palladium II; on the other hand it is well known that platinum IV, as $PtCl_6''$, reacts with quinolines to precipitate temperature dependent ionic complexes, $(quinoline\ H)_2PtCl_6$.

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THE HEMICELLULOSE OF THE FOSSILIZED WOOD OF CEDRUS PENHALLOWII

By J. K. N. Jones and E. Merler

We were supplied with a sample of holocellulose from wood of a prehistoric tree, *Cedrus penhallowii*, through the kindness of Dr. J. R. W. Vallentyne of Queen's University and Dr. E. S. Barghoon of Harvard University. The residual holocellulose, prepared by extracting the extractive free wood with sodium chlorite followed by ammonia, was a white powder which contained relatively large amounts of silica.

The holocellulose was extracted with a cold potassium hydroxide – borate solution (20:4% w/v) in order to remove the hemicellulose fraction. The insoluble residue gave on hydrolysis glucose and traces of mannose. On addition of Fehling reagent to an aqueous solution of the extract, two fractions were obtained. The insoluble copper complex (70%) was decomposed with dilute acid and precipitated by the addition of alcohol. The resulting white powder gave on hydrolysis a mixture of sugars—glucose, mannose, xylose, and glucuronic acid. The fraction (5%) which did not form a copper complex was isolated after acidification with glacial acetic acid and precipitation by the addition of alcohol. On hydrolysis this fraction gave glucose. The sugars were detected chromatographically.

This wood, which grew in the Myocene era and which may be 10–20 million years old, contains a hemicellulose which seems not to differ greatly from that found in living softwoods. However, 4-*O*-methyl-D-glucuronic acid, which was not detected in the hydrolyzate from the prehistoric wood, is present in many softwoods of recent origin.

Methylation studies are in progress on these materials.

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4,6-*O*-*iso*PROPYLIDENE-METHYL-α-D-GLUCOSIDE

By J. K. N. Jones

When acetone condenses with sugars and sugar glycosides a five-membered ring ketal is usually formed (cf. 1,2-mono- and 1,2:5,6-di-*O*-*iso*propylidene-D-glucose, 2,3-*O*-*iso*propylidene-methyl-α-D-mannoside (1), and 3,4-*O*-*iso*propylidene-methyl-β-D-galactoside), but when a primary alcohol group is engaged in ring formation a six-membered ring may result. For example L-sorbose yields 2,3:4,6-di-*O*-*iso*propylidene-L-sorbose and D-xylose gives 1,2:3,5-di-*O*-*iso*propylidene-D-xylose, but D-mannose on condensation with acetone yields the 2,3:5,6-di-*O*-*iso*propylidene derivative.

Methyl-α-D-glucoside will also give a 4,6-*O*-*iso*propylidene derivative (two six-membered rings with a *trans* junction); cf. (1, p. 1019). This is not unexpected since the hydroxyl groups on C_4 and C_6 of both the mannoside and glucoside are similarly situated. Acetone thus behaves like aldehydes in that it can yield six-membered rings on condensation with sugar derivatives (3, 4, 5).

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The structure of the *O-iso*propylidene derivative of methyl-α-D-glucoside was proved in the following manner. It gave a 2,3-di-*O*-tosyl, a 2,3-di-*O*-mesyl, a 2,3-di-*O*-benzoyl, and a 2,3-di-*O*-methyl derivative the structure of which was proved because it could be hydrolyzed to the known 2,3-di-*O*-methyl-α-D-glucoside. The original 4,6-*O-iso*propylidene derivative was hydrolyzed by dilute acetic acid, with the regeneration of methyl-α-D-glucoside, and was oxidized by sodium *meta*periodate thus proving that it possessed hydroxyl groups on adjacent carbon atoms.

EXPERIMENTAL

4,6-O-Isopropylidene-methyl-α-D-glucoside

Methyl-α-D-glucoside (10 gm.) was added to a solution of anhydrous zinc chloride (30 gm.) in acetone (200 ml.) and the mixture was boiled under reflux until a clear solution resulted (overnight). The cooled solution was poured onto a mixture of ice and a saturated solution of sodium carbonate. When all the ice had melted the solution was filtered and the alkaline filtrate concentrated under reduced pressure to *ca.* 250 ml. The cooled concentrate was then exhaustively extracted with chloroform. Concentration of the chloroform extract yielded 4,6-*O-iso*propylidene-methyl-α-D-glucoside (5.5 gm.) as a sirup which slowly crystallized. The crude product was crystallized with difficulty from benzene or from acetone – ether – light petroleum (b.p. 60–110°C.) mixture. It usually separated as a jelly which crystallized on standing. Sometimes crystalline material was obtained without the intermediate formation of jelly. The pure product (3.5 gm.) had m.p. 84–86°C., $[\alpha]_D$ +94°C. (c. 5.0, in water), and on hydrolysis with hot dilute acetic acid gave acetone, detected by its odor and by the sodium nitroprusside test, and methyl-α-D-glucoside, m.p. and mixed m.p. 168°C. Anal. Calc. for $C_{10}H_{18}O_6$: C, 51.2; H, 7.7; OMe, 13.3. Found: C, 50.9; H, 7.8; OMe, 13.6.

2,3-Di-O-methyl-4,6-O-isopropylidene-methyl-α-D-glucoside

The *iso*propylidene derivative on methylation with Purdie's reagents gave the corresponding 2,3-di-*O*-methyl ether in quantitative yield. This product sublimed at 100°C. It was readily recrystallized from ether – light petroleum (b.p. 60–110°C.) mixture, m.p. 80°C. Anal. Calc. for $C_{12}H_{22}O_6$: C, 54.9;H, 8.4; OMe, 35.5. Found: C, 55.0; H, 8.8; OMe, 35.0. When this substance was boiled with 50% acetic acid, acetone was produced and evaporation of the solvent left 2,3-di-*O*-methyl-methyl-α-D-glucoside, m.p. 83–84°C. (lit. 83–85°C. (2)).

2,3-Di-O-methanesulphonyl and 2,3-Di-O-toluene-p-sulphonyl 4,6-O-Isopropylidene-methyl-α-D-glucoside

The *iso*propylidene derivative (0.1 gm.) was dissolved in pyridine (10 ml.) and methanesulphonyl chloride (0.5 ml.) was added. The mixture became warm (40°C.) and was then allowed to stand at 20°C. for 20 hr. The solution was poured onto ice and the methanesulphonyl derivative isolated by extraction of the solution with chloroform in the usual manner. The product (0.1 gm.) was recrystallized from aqueous alcohol, m.p. 87°C. Anal. Calc. for $C_{12}H_{22}O_{10}S_2$: C, 36.9; H, 5.6; S, 16.4. Found: C, 36.8; H, 5.6; S, 16.4.

The 2,3-di-*O*-toluene-*p*-sulphonate was prepared in a similar fashion from the *iso*propylidene derivative (0.1 gm.), pyridine (10 ml.), and toluene-*p*-sulphonyl chloride (1.0 gm.). The product was recrystallized from methanol, m.p. 145°C. Anal. Calc. for $C_{24}H_{30}O_{10}S_2$: C, 53.2; H, 5.6; OMe, 11.8. Found: C, 53.3; H, 5.6; OMe, 11.8.

2,3-Di-O-benzoyl-4,6-O-isopropylidene-methyl-α-D-glucoside

The *iso*propylidene derivative of methyl-α-D-glucoside (2.1 gm.) was dissolved in pyridine (30 ml.) and benzoyl chloride (5 ml.) added. The solution became warm and pyridine hydrochloride began to separate. After 12 hr., water (5 ml.) was added and the mixture poured onto ice. The 2,3-di-*O*-benzoyl derivative was isolated by extraction of the solution with chloroform. The product was recrystallized from acetone methanol. Yield: 2.8 gm., 70%; m.p. 131°C. Anal. Calc. for $C_{24}H_{26}O_8$: C, 65.2; H, 6.0. Found: C, 65.3; H, 6.1.

Oxidation of 4,6-O-Isopropylidene-methyl-α-D-glucoside with Sodium Metaperiodate

The substance (0.248 gm.) was dissolved in water (5 ml.), a solution of sodium *meta*periodate (5 ml., 0.25 *M*) added, and the change in optical rotation observed. $[\alpha]_D$ +92° (3 min.); +88° (4 min.); +71° (15 min.); +62° (25 min.); +46° (65 min.); +48° (120 min.); +57° (180 min.); +82° (20 hr.) constant value. At the stage of minimum optical rotation approximately one mole of periodate had been consumed per mole of sugar derivative.

ACKNOWLEDGMENT

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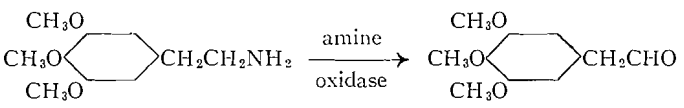
THE SYNTHESIS OF 3,4,5-TRIMETHOXYPHENYLACETALDEHYDE[1]

BY J. G. DUFF AND J. M. PEPPER

As part of a more general program of research concerned with a biochemical study of the hallucinogenic activity of mescaline (I), it was necessary to prepare 3,4,5-trimethoxyphenylacetaldehyde (II). If the primary action of this drug were the deamination by an amine oxidase:



I II

[1]*This note constitutes part of a thesis submitted by J. G. Duff for the degree of Master of Science in Pharmacy, March, 1955.*

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THE HEMICELLULOSE OF THE FOSSILIZED WOOD OF CEDRUS PENHALLOWII

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This wood, which grew in the Myocene era and which may be 10–20 million years old, contains a hemicellulose which seems not to differ greatly from that found in living softwoods. However, 4-*O*-methyl-D-glucuronic acid, which was not detected in the hydrolyzate from the prehistoric wood, is present in many softwoods of recent origin.

Methylation studies are in progress on these materials.

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4,6-*O*-*iso*PROPYLIDENE-METHYL-α-D-GLUCOSIDE

By J. K. N. Jones

When acetone condenses with sugars and sugar glycosides a five-membered ring ketal is usually formed (cf. 1,2-mono- and 1,2:5,6-di-*O*-*iso*propylidene-D-glucose, 2,3-*O*-*iso*propylidene-methyl-α-D-mannoside (1), and 3,4-*O*-*iso*propylidene-methyl-β-D-galactoside), but when a primary alcohol group is engaged in ring formation a six-membered ring may result. For example L-sorbose yields 2,3:4,6-di-*O*-*iso*propylidene-L-sorbose and D-xylose gives 1,2:3,5-di-*O*-*iso*propylidene-D-xylose, but D-mannose on condensation with acetone yields the 2,3:5,6-di-*O*-*iso*propylidene derivative.

Methyl-α-D-glucoside will also give a 4,6-*O*-*iso*propylidene derivative (two six-membered rings with a *trans* junction); cf. (1, p. 1019). This is not unexpected since the hydroxyl groups on C_4 and C_6 of both the mannoside and glucoside are similarly situated. Acetone thus behaves like aldehydes in that it can yield six-membered rings on condensation with sugar derivatives (3, 4, 5).

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The 2,3-di-*O*-toluene-*p*-sulphonate was prepared in a similar fashion from the *iso*propylidene derivative (0.1 gm.), pyridine (10 ml.), and toluene-*p*-sulphonyl chloride (1.0 gm.). The product was recrystallized from methanol, m.p. 145°C. Anal. Calc. for $C_{24}H_{30}O_{10}S_2$: C, 53.2; H, 5.6; OMe, 11.8. Found: C, 53.3; H, 5.6; OMe, 11.8.

2,3-Di-O-benzoyl-4,6-O-isopropylidene-methyl-α-D-glucoside

The *iso*propylidene derivative of methyl-α-D-glucoside (2.1 gm.) was dissolved in pyridine (30 ml.) and benzoyl chloride (5 ml.) added. The solution became warm and pyridine hydrochloride began to separate. After 12 hr., water (5 ml.) was added and the mixture poured onto ice. The 2,3-di-*O*-benzoyl derivative was isolated by extraction of the solution with chloroform. The product was recrystallized from acetone methanol. Yield: 2.8 gm., 70%; m.p. 131°C. Anal. Calc. for $C_{24}H_{26}O_8$: C, 65.2; H, 6.0. Found: C, 65.3; H, 6.1.

Oxidation of 4,6-O-Isopropylidene-methyl-α-D-glucoside with Sodium Metaperiodate

The substance (0.248 gm.) was dissolved in water (5 ml.), a solution of sodium *meta*periodate (5 ml., 0.25 *M*) added, and the change in optical rotation observed. $[\alpha]_D$ +92° (3 min.); +88° (4 min.); +71° (15 min.); +62° (25 min.); +46° (65 min.); +48° (120 min.); +57° (180 min.); +82° (20 hr.) constant value. At the stage of minimum optical rotation approximately one mole of periodate had been consumed per mole of sugar derivative.

ACKNOWLEDGMENT

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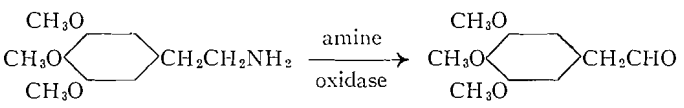
THE SYNTHESIS OF 3,4,5-TRIMETHOXYPHENYLACETALDEHYDE[1]

BY J. G. DUFF AND J. M. PEPPER

As part of a more general program of research concerned with a biochemical study of the hallucinogenic activity of mescaline (I), it was necessary to prepare 3,4,5-trimethoxyphenylacetaldehyde (II). If the primary action of this drug were the deamination by an amine oxidase:



I II

[1]*This note constitutes part of a thesis submitted by J. G. Duff for the degree of Master of Science in Pharmacy, March, 1955.*

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then the resulting aldehyde might be considered to show a similar if not even an enhanced activity.

One prior synthesis of this aldehyde has been reported, that by Mauthner (1) who obtained it by the ozonolysis of 3,4,5-trimethoxyallylbenzene. In this work the following alternative synthetic routes were followed:

1. 3,4,5-Trimethoxyallylbenzene was hydroxylated with cold potassium permanganate and the resulting diol was oxidized with either periodic acid or lead tetraacetate to produce the required aldehyde (II).

2. 3,4,5-Trimethoxybenzaldehyde was converted to the homoaldehyde (II) by the application of the Darzens glycidic ester condensation procedure.

From both syntheses the required 3,4,5-trimethoxyphenylacetaldehyde was obtained, after distillation, as a white crystalline solid, m.p. 39–40°C., although previously reported by Mauthner (1) to be an oil.

EXPERIMENTAL[2]

Method 1

3,4,5-Trimethoxyallylbenzene

4-Hydroxy-3,5-dimethoxyallylbenzene, which had been prepared from 2,6-dimethoxyphenol according to the method of Pearl (3), was methylated with dimethyl sulphate in alkali to produce 3,4,5-trimethoxyallylbenzene.

3-(3′,4′,5′-Trimethoxyphenyl)propanediol-1,2

The most satisfactory conditions found for the hydroxylation of 3,4,5-trimethoxyallylbenzene were as follows. 3,4,5-Trimethoxyallylbenzene (20.8 gm.) was dissolved in a mixture of water (100 ml.) and ethanol (200 ml.). Potassium permanganate (5.5 gm.), dissolved in water (1100 ml.), was added in one portion with stirring, the temperature being maintained below 15°C. After three minutes the manganese dioxide was removed by filtration and the aqueous solution concentrated to a volume of 400 ml. This solution was extracted with benzene in a continuous liquid–liquid extractor for an extended length of time. From the resulting benzene extract the crude 3-(3′,4′,5′-trimethoxyphenyl)propanediol-1,2 was obtained by concentration. After recrystallization from benzene – petroleum ether (Skellysolve C), yield 12.2 gm. (52.6%), m.p. 83–84°C. Calc for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49%. Found: C, 59.48; H, 7.46%.

Oxidation of 3-(3′,4′,5′-Trimethoxyphenyl)propanediol-1,2

(*a*) *Using periodic acid.*—3-(3′,4′,5′-Trimethoxyphenyl)propanediol-1,2 (6.4 gm.) was dissolved in water (300 ml.). Paraperiodic acid (3.7 gm.) was dissolved in water (200 ml.) and this solution added dropwise to the former. After 30 min., lead nitrate (10%, 100 ml.) was added and the precipitate removed by filtration. The filtrate was extracted with ether (5×50 ml.) and then with benzene (50 ml.). The combined extracts were dried over anhydrous sodium sulphate and the solvents removed. Distillation (bath temperature, 160–190°C. at 0.05 mm.) of the residue yielded 3,4,5-trimethoxyphenylacetaldehyde (1.85 gm., 31.1%) as a viscous pale yellow oil which readily

[2]*All melting points are uncorrected.*

crystallized on seeding, m.p. 39–40°C.; semicarbazone, m.p. 186–187°C., reported m.p. 188°C. (1).

(*b*) *Using lead tetraacetate.*—3-(3′,4′,5′-trimethoxyphenyl)propanediol-1,2 (5 gm.) was dissolved in dry benzene (55 ml.) and placed in a three-necked flask provided with a magnetic stirrer and condenser. Under reflux, lead tetraacetate (9.3 gm.) was added in small portions. After completion of the addition, the mixture was refluxed for 10 min. After cooling, the mixture was filtered, the benzene washed with water, dried, and removed by distillation. The residue was distilled (bath temperature, 160–190°C. at 0.05 mm.) to yield 3,4,5-trimethoxyphenylacetaldehyde (2.2 gm., 50.9%) as a viscous pale yellow oil which crystallized on seeding, m.p. 39–40°C.; semicarbazone, m.p. 186–188°C.

Method 2

Darzens Glycidic Ester Condensation (2)

From 3,4,5-trimethoxybenzaldehyde (14.8 gm.), prepared in a 75.6% yield by the methylation of syringaldehyde, and ethyl chloroacetate (9.0 gm.) with sodium ethoxide as a catalyst, there was obtained the white intermediate glycidic ester which, after recrystallization from water–ethanol, weighed 4.0 gm. This solid was added to a solution of hydrochloric acid (1.3 ml.) and water (6.8 ml.) in a flask fitted with a reflux condenser, and when it was gently warmed, gas was evolved and an oily layer separated. After one and one-half hours, the reaction mixture was cooled and extracted with benzene. This extract was washed with water (20 ml.), dried over anhydrous sodium sulphate, and concentrated to remove the solvent. Distillation (bath temperature, 160–190°C. at 0.05 mm.) of the residue yielded 3,4,5-trimethoxyphenylacetaldehyde (0.6 gm., 3.7%) as a clear viscous oil which readily crystallized, m.p. 39–40°C. Calc. for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71%. Found: C, 62.07; H, 6.56%. The semicarbazone melted at 187–188°C.

A mixed melting point between samples of the semicarbazones prepared from the 3,4,5-trimethoxyphenylacetaldehydes made by each method showed no depression, being at 187–188°C.

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SYNTHESIS OF 2,5,6-TRI-*O*-METHYL-D-GLUCOSE[1]

BY C. T. BISHOP AND J. SCHMORAK[2]

ABSTRACT

The previously unknown 2,5,6-tri-*O*-methyl-D-glucose has been prepared from D-glucose. Proof of the constitution of this new sugar derivative is based on its chemical reactions and method of synthesis.

INTRODUCTION

Among the 10 possible isomeric tri-*O*-methyl-D-glucoses the 2,5,6-tri-*O*-methyl derivative has not been reported (1). The synthesis and characterization of this new tri-*O*-methyl ether of D-glucose are described in this report.

The synthesis was accomplished by classical methods of carbohydrate chemistry using non-migratory benzyl and *iso*propylidene groups to block specific hydroxyl groups. D-Glucose was converted to the well-characterized, crystalline, 1,2-*O*-*iso*propylidene-3-*O*-benzyl-5,6-di-*O*-acetyl-D-glucofuranose (I) by a series of reactions previously described (2, 3, 6). Methylation of I by dimethyl sulphate and alkali yielded the 5,6-di-*O*-methyl derivative (II) which was hydrolyzed (III), methanolyzed (IV), and methylated by Purdie's reagents (8) to give methyl-2,5,6-tri-*O*-methyl-3-*O*-benzyl-(α,β)-D-glucofuranoside (V). Removal of the *iso*propylidene group from II was surprisingly difficult requiring hydrolysis with aqueous acid for 10 hr. Two steps were therefore required to obtain IV from II instead of the more usual direct methanolysis of the *iso*propylidene group. The 3-*O*-benzyl group was removed from V by reduction and the methyl glucoside (VI) was hydrolyzed by acid to give the free sugar (VII).

The 2,5,6-tri-*O*-methyl-D-glucose was obtained as a colorless sirup which has not crystallized. The new tri-*O*-methyl-D-glucose has been characterized by conversion to crystalline 2,5,6-tri-*O*-methyl-D-gluconamide.

Proof of constitution of the 2,5,6-tri-*O*-methyl-D-glucose followed from the method of synthesis and was supported by the chemical reactions of the sugar. Salmon and Powell (9) prepared 5,6-di-*O*-methyl-D-glucose by methylation of 1,2-*O*-*iso*propylidene-3-*O*-benzoxymethyl-D-glucose and removal of the blocking groups. The structure of this 5,6-di-*O*-methyl-D-glucose was well established

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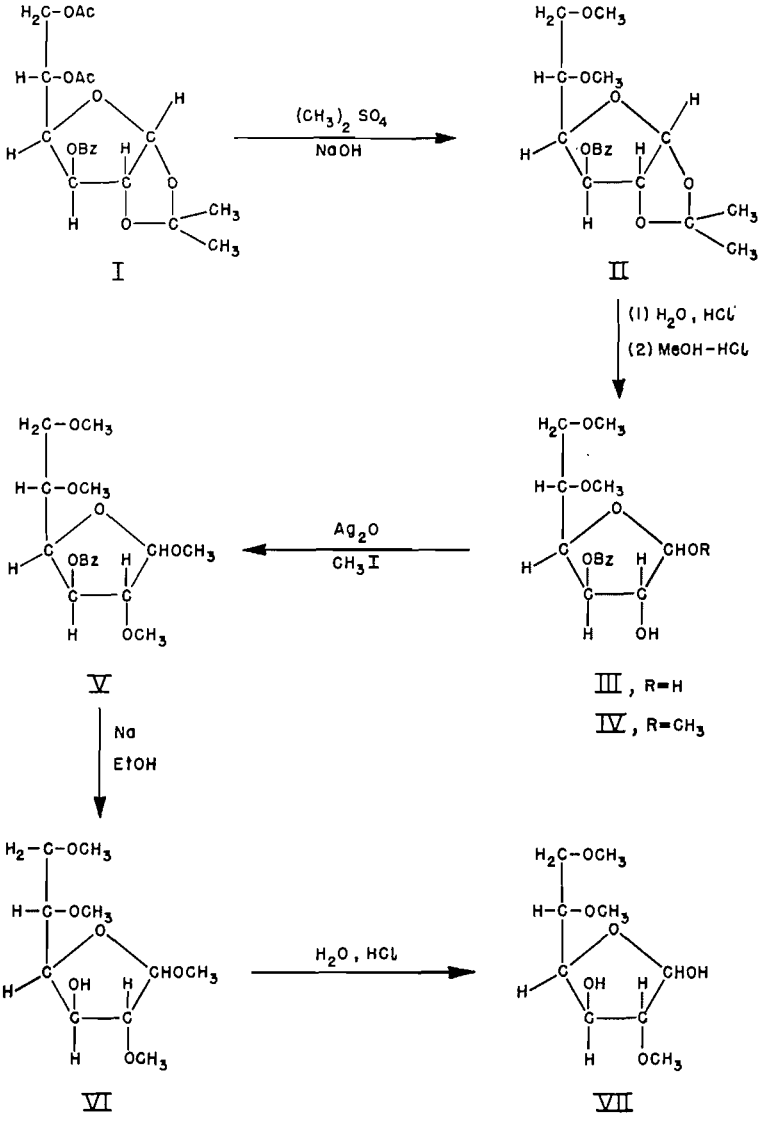
[2]*National Research Council Postdoctorate Fellow 1954–56.*

by the identification of di-*O*-methyl glyceraldehyde as a product of periodate oxidation of the sugar. Freudenberg and Plankenhorn (5) prepared the same di-*O*-methyl-D-glucose by methylation of 1,2-*O*-*iso*propylidene-3-*O*-benzyl-5,6-di-*O*-acetyl-D-glucose (I), the starting material used in the present synthesis.



I II III, R=H IV, R=CH3 V VI VII

There can be little doubt then that in compound II two methyl ether groups were present in positions 5 and 6. The tri-*O*-methyl-D-glucose (VII) yielded a furanolactone when oxidized by bromine, showing that position 4 was involved in ring formation. After replacement of the 1,2-*O*-*iso*propylidene group by a methyl glycoside (IV) only position 2 was open to methylation. The presence of a methyl ether at position 2 in the final product was confirmed by (*a*) its

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failure to give a phenylosazone or *p*-bromophenylosazone, and (*b*) a negative Weerman (10) test given by the derived tri-*O*-methyl-D-gluconamide. It was clear, therefore, that the product of this synthesis could only be 2,5,6-tri-*O*-methyl-D-glucose.

EXPERIMENTAL

Chromatographic separations were carried out in the following solvent systems: (*A*) butanol: ethanol: water—5: 1: 4, (*B*) methyl ethyl ketone: water—2: 1. Sugars were detected on the papers by aniline oxalate spray reagent (7). Evaporations were done under diminished pressure at 40° C. or less. All melting points are corrected and boiling points are bath temperatures. Specific rotations are equilibrium values unless otherwise stated. Yields are calculated on the preceding compound.

*1,2-O-Isopropylidene-3-O-benzyl-5,6-di-O-acetyl-*D*-glucofuranose* (*I*)

This compound was prepared from D-glucose by the following series of reactions, previously described by Freudenberg and his co-workers (2, 3, 6). D-Glucose was condensed with acetone to give 1,2;5,6-di-*O-iso*propylidene-D-glucofuranose which was then benzylated yielding 1,2;5,6-di-*O-iso*propylidene-3-*O*-benzyl-D-glucofuranose. Partial hydrolysis of this compound removed the 5,6-*O-iso*propylidene group, yielding sirupy 1,2-*O-iso*propylidene-3-*O*-benzyl-D-glucofuranose, which was acetylated to give the well-characterized, crystalline 1,2-*O-iso*propylidene-3-*O*-benzyl-5,6-di-*O*-acetyl-D-glucofuranose. This compound had m.p. 119.5–120° C. and $[\alpha]_D^{23} = -52°$ ($c = 2.10$ in tetrachloroethane). Reported (2) values for the same compound are m.p. 119–119.5° C. and $[\alpha]_D = -53°$ (in tetrachloroethane). Analysis: Calc. for $C_{20}H_{26}O_8$: C, 60.88%; H, 6.68%. Found: C, 61.11%; H, 6.75%.

*1,2-O-Isopropylidene-3-O-benzyl-5,6-di-O-methyl-*D*-glucofuranose* (*II*)

Methylation of compound I with dimethyl sulphate and alkali as previously described (5) gave II in 87.6% yield. The product had $[\alpha]_D^{25} = -16°$ ($c = 8.52$ in acetone), in good agreement with the reported (5) value, $[\alpha]_D^{20} = -15.8°$ ($c = 1$ in acetone). Analysis: Calc. for $C_{18}H_{26}O_6(2 \times OCH_3)$: OCH_3, 18.3%. Found OCH_3, 16.8%.

*3-O-Benzyl-5,6-di-O-methyl-*D*-glucofuranose* (*III*)

Compound II (81.4 gm.) was dissolved in ethanol (300 ml.) and 6% aqueous hydrochloric acid (300 ml.) was added. The solution was boiled under reflux for 14 hr., cooled, and neutralized with silver carbonate. Silver salts were filtered and the filtrate was evaporated to a sirup from which water was removed by azeotropic distillation with ethanol. The residual sirup was dried to a constant weight of 65.1 gm. (76.3% yield). The infrared spectrum of this sirup did not contain either of the absorption peaks at 1375 $cm.^{-1}$ or 1170 $cm.^{-1}$ assigned to *iso*propylidene groups. Both of these peaks were present in the infrared spectra of compounds I and II. Infrared analysis was also used to establish the conditions required to remove the *iso*propylidene groups. In preliminary experiments when hydrolyses were stopped at 6, 8, and 10 hr., the products still showed the characteristic *iso*propylidene absorption peaks in

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the infrared spectra. Because of the drastic conditions required to remove the *iso*propylidene group, the methyl glucoside (IV) was formed from II in two steps instead of direct methanolysis.

Compound III decomposed during attempted distillation and was not purified to any further extent. Analysis: Calc. for $C_{15}H_{22}O_6$ ($2 \times OCH_3$): OCH_3, 20.8%. Found OCH_3, 22.0%.

Methyl-3-O-benzyl-5,6-di-O-methyl-(α,β)-D-*glucofuranoside* (IV)

Compound III (50.2 gm.) was dissolved in 5% anhydrous methanolic hydrogen chloride (500 ml.) and the solution was allowed to stand till no further reducing power could be detected by aniline oxalate spray reagent. Acid was neutralized by silver carbonate, the silver salts were filtered, and the filtrate was evaporated to a sirup which was dried to constant weight (36.8 gm., 69.9% yield) over phosphorus pentoxide at 0.02 mm. A sample was distilled for analysis; b.p. 145–148° C. at 0.05 mm., $[\alpha]_D^{24} = +12°$ ($c = 3.40$ in ethanol), no mutarotation. Analysis: Calc. for $C_{16}H_{24}O_6$ ($3 \times OCH_3$): C, 61.52%; H, 7.74%; OCH_3, 29.8%. Found: C, 61.72%; H, 7.60%; OCH_3, 28.0%.

Methyl-2,5,6-tri-O-methyl-3-O-benzyl-(α,β)-D-*glucofuranoside* (*V*)

A solution of IV (36.8 gm.) in methyl iodide (300 ml.) was boiled under reflux during the addition of eight 5 gm. portions of silver oxide (8). The additions were made at one-half hour intervals. Silver salts were filtered, washed with acetone, and the filtrate was evaporated to a sirup which was methylated three more times by the same procedure. The sirupy product was dried to constant weight over phosphorus pentoxide at 0.02 mm. (33.5 gm., 87.2% yield). The characteristic absorption band of hydroxyl groups at 3500 cm.$^{-1}$ was barely evident in the infrared spectrum of this product. A sample was distilled for analysis, b.p. 151–156° C. at 0.08 mm., $[\alpha]_D^{20} = +6°$ ($c = 4.03$ in ethanol). Analysis: Calc. for $C_{17}H_{26}O_6$ ($3 \times OCH_3$): C, 62.56%; H, 8.03%; OCH_3, 38.0%. Found: C, 61.98%; H, 7.76%; OCH_3, 37.5%.

Methyl-2,5,6-tri-O-methyl-(α,β)-D-*glucofuranoside* (*VI*)

Compound V (33.5 gm.) was reductively debenzylated by sodium (50 gm.) in ethanol (500 ml.), a method used by Freudenberg and Plankenhorn (4) in their synthesis of 2,4,6-tri-*O*-methyl-D-glucopyranose. Four such debenzylations were required to remove the absorption peak at 1500 cm.$^{-1}$ in the infrared spectrum. This absorption band is characteristic of benzyl groups and was present in the spectrum of V. The debenzylated product was a dark colored sirup (25 gm.) which was distilled, b.p. 130–132° C. at 0.14 mm. giving 16.2 gm. (65.6% yield) of VI, $[\alpha]_D^{20} = -1°$ ($c = 5.1$ in chloroform). Analysis: Calc. for $C_{10}H_{20}O_6$ ($3 \times OCH_3$): C, 50.83%; H, 8.53%; OCH_3, 52.53%. Found: C, 52.11%; H, 8.21%; OCH_3, 47.4%.

This analysis showed that the compound was not pure but contained small amounts of di-*O*-methyl or monomethyl derivative. These compounds could have arisen from incomplete methylation, or more probably, because of the correct analysis of V, from reductive de-etherification during the debenzyl-

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ations. Because the reducing sugar, obtained by hydrolysis of this impure glucoside, could be separated very easily by chromatographic methods no further attempt was made to purify VI.

2,5,6-Tri-O-methyl-D-glucofuranose (VII)

The methyl glucoside (VI) was boiled under reflux in 0.5 *N* hydrochloric acid for three and one half hours. The acid was neutralized with silver carbonate, silver salts were filtered, and the filtrate was evaporated to a sirup. Chromatographic examination of this product in solvents A and B revealed the presence of minor components which moved more slowly than the main fraction. The R_G (rate of movement relative to 2,3,4,6-tetra-*O*-methyl-D-glucose) value of the main component was 0.88 in solvent A. From time to time, as samples were required for analysis and derivative formation, portions of the crude tri-*O*-methyl-D-glucose were purified by preparative paper chromatography on Whatman 3MM paper using solvent B. The recovery of pure 2,5,6-tri-*O*-methyl-D-glucofuranose corresponded to 46% yield based on VI or 12.4% based on I. A sample was distilled for analysis, b.p. 155–160° C. at 0.038 mm., $[\alpha]_D^{26} = +11°$ ($c = 4.72$ in water). Analysis: Calc. for $C_9H_{18}O_6$ ($3 \times OCH_3$): C, 48.64%; H, 8.16%; OCH_3, 41.9%. Found: C, 47.95%; H, 7.97%; OCH_3, 41.7%.

Characterization of 2,5,6-Tri-O-methyl-D-glucofuranose

Repeated attempts to form a phenylosazone or *p*-bromophenylosazone from the tri-*O*-methyl-D-glucose were unsuccessful, indicating the presence of a methyl ether at position 2.

A sample (320 mgm.) of the chromatographically pure tri-*O*-methyl-D-glucose (VII) was dissolved in water (3 ml.) and oxidized by bromine (0.75 ml.) in the presence of barium carbonate (150 mgm.) for 18 hr. Hydrochloric acid (12%) was added till the solution was acid and bromine was then removed by aeration. The resulting clear aqueous solution was extracted continuously with chloroform till no more material was removed. The chloroform extract was dried (sodium sulphate) and evaporated to a sirup (292 mgm.). The sirupy acid was lactonized by heating at 0.15 mm. and 100° C. for one hour. The lactone showed the slow mutarotation in water characteristic of furanolactones, $[\alpha]_D^{26} = +67° \rightarrow +62°$ in 71 hr. ($c = 1.13$ in water). Analysis: Calc. for $C_9H_{16}O_6$ ($3 \times OCH_3$): OCH_3, 42.5%. Found OCH_3, 41.7%.

The 2,5,6-tri-*O*-methyl-D-glucono-γ-lactone (250 mgm.) was dissolved in anhydrous methanol and anhydrous ammonia was passed through the solution for one-half hour. The ammoniacal solution was stored at 5° C. for three days and was then evaporated slowly in a desiccator. The amide crystallized as fine needles and was recrystallized from hot ethyl acetate to a constant melting point of 116.5–117° C. (yield, 113.3 mgm.). The 2,5,6-tri-*O*-methyl-D-gluconamide was stable in aqueous solution showing no mutarotation after 48 hr., $[\alpha]_D^{26} = +40°$ ($c = 2.37$ in water), and a Weerman test (10) for α-hydroxy amides was negative. Analysis: Calc. for $C_9H_{19}O_6N$ ($3 \times OCH_3$): C, 45.54%; H, 8.08%; N, 5.91%; OCH_3, 39.2%. Found: C, 45.86%; H, 8.14%; N, 6.05%; OCH_3, 39.1%.

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THE FRIES REARRANGEMENT OF PHENYL ISOBUTYRATE[1]

By T. I. Briggs,[2] G. G. S. Dutton, and E. Merler[3]

ABSTRACT

Phenyl isobutyrate has been found to undergo a normal Fries rearrangement with anhydrous aluminum chloride at 140°C. to give a mixture of 2-hydroxy- (40%) and 4-hydroxy-isobutyrophenone (11%). When the reaction was carried out in nitrobenzene solution at room temperature the 4-isomer was formed in 86% yield. Methylation of these compounds furnished 2- and 4-methoxy-isobutyrophenone, identical with the compounds obtained by direct acylation of anisole. Reduction of the hydroxy-isobutyrophenones, which were also prepared by direct acylation of phenol, afforded an alternative route to the isobutylphenols. The orientation of each methoxy ketone was verified by oxidation to the corresponding acid.

INTRODUCTION

The literature pertaining to the Fries rearrangment has been well documented (3, 4) but these reviews make no mention of the reaction having been applied to esters of phenol in which the acyl group has a branched carbon chain. Since 2-isobutylphenol and 4-isobutylphenol were required as part of a program investigating herbicidal activity of dinitrophenols, their preparation was considered by subjecting phenyl isobutyrate to a Fries rearrangement and reducing the hydroxy ketones thus formed according to the method of Clemmensen (5) as modified by Martin (10).

Examination of the literature revealed very little information on 2-hydroxy- or 2-methoxy-isobutyrophenone, although the corresponding 4-isomers, being readily accessible by direct acylation, have been more fully described. In the course of a series of experiments on the reaction between ferric chloride and phenols, Huber and Brunner (8) found that anhydrous ferric chloride converted phenyl isobutyrate into a mixture of 2- and 4-hydroxy-isobutyrophenone. No yield was quoted for the 2-isomer, which was identified as the oxime, and the 4-isomer was obtained in 16% yield but no derivatives were prepared; the latter was oxidized to 4-hydroxybenzoic acid thus determining the orientation. The work of these authors appears to be the only reference to 2-hydroxy-isobutyrophenone. The results described in the present paper show that when phenyl isobutyrate is reacted with anhydrous aluminum chloride at 140–150°C. for one hour 2-hydroxy-isobutyrophenone is formed in 40% yield and the 4-isomer in 11% yield. These results and the constants of the two isomers agree well with those quoted by Huber and Brunner (8). We have also found that when phenyl isobutyrate is reacted with aluminum chloride in nitrobenzene solution at room temperature 4-hydroxy-isobutyrophenone is formed in 86% yield (1). Both isomers on reduction by Clemmensen's method give the corresponding isobutylphenol, identical with authentic specimens prepared by an alternative route (6).

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The only reference to 2-methoxy-isobutyrophenone is in a paper by Vavon and Décombe (13) in which they report the preparation of this compound by reaction of the Grignard reagent of 2-bromoanisole with isobutyryl chloride. They describe the compound as a solid melting at 96–98°C. but were unable to form an oxime. We have prepared 2-methoxy-isobutyrophenone by two methods. In one case the hydroxy ketone obtained from the Fries rearrangement of phenyl isobutyrate was methylated with dimethyl sulphate and in the other case anisole was acylated directly with isobutyryl chloride. The 2-methoxy-isobutyrophenone, prepared by either route, has so far remained as an oil, but readily formed a crystalline 2,4-dinitrophenylhydrazone and a crystalline oxime. Portions of the 2- and 4-methoxy-isobutyrophenones were oxidized with alkaline permanganate to 2-methoxybenzoic and anisic acids, thus confirming the orientation of the substituents. In view of recent work (7) on the anomalous reactivity of 2-methoxyphenylmagnesium halides there must be some doubt whether the compound isolated by Vavon and Décombe was 2-methoxy-isobutyrophenone, owing to the lack of supporting evidence.

EXPERIMENTAL*

Phenyl Isobutyrate

Isobutyryl chloride (106 gm., 1.0 mole), prepared from redistilled thionyl chloride and isobutyric acid in 95% yield by a standard procedure (9), was gradually added at room temperature to phenol (104 gm., 1.1 moles) when hydrogen chloride was vigorously evolved. The crude ester, obtained by distillation, was cooled to 0°C., repeatedly washed with ice-cold potassium hydroxide solution (1 *N*), and dried over solid potassium hydroxide, the flask being constantly immersed in an ice bath. Fractionation gave phenyl isobutyrate (161 gm., 81%) as a clear liquid boiling at 211°C. and having n^{25}, 1.4919. Literature (2), 112°C. (25.5 mm.).

High Temperature Fries Rearrangement of Phenyl Isobutyrate

Anhydrous aluminum chloride (21.5 gm., 0.16 mole) was placed in a 500 ml. flask and heated to 70°C. Phenyl isobutyrate (20 gm., 0.10 mole) was added in small portions over a period of 10 to 15 min. with stirring. A vigorous evolution of hydrogen chloride occurred and the temperature rose to about 100°C. When the addition of ester was complete the temperature was rapidly raised to 140–150°C. and maintained between these limits for one hour. The reaction mixture was cooled to room temperature and the glassy solid decomposed by the addition of hydrochloric acid (100 ml., 6 *N*). After the solution was heated for five minutes on the steam cone in order to complete the hydrolysis, the viscous red oil was separated and washed with warm hydrochloric acid (30 ml., 6 *N*) and two portions of warm water. Distillation of the oil *in vacuo* yielded two fractions which were separately redistilled.

Fraction 1, identified as 2-hydroxy-isobutyrophenone, distilled as a clear liquid (8.0 gm., 40%) boiling at 68°C. (0.4 mm.) and having n^{25}, 1.5367. Literature (8) 110°C. (10 mm.). *2,4-Dinitrophenylhydrazone*, m.p. 186°C.

**All melting and boiling points are uncorrected.*

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(decomp.). Anal. calc. for $C_{16}H_{16}O_5N_4$: N, 16.2%. Found: N, 16.3%. *Semicarbazone*, m.p. 178°C. Anal. calc. for $C_{11}H_{15}O_2N_3$: N, 19.0%. Found: N, 19.1%. *Oxime*, m.p. 126°C.; literature (8), m.p. 129°C. Anal. calc. for $C_{10}H_{13}O_2N$: N, 7.8%. Found: N, 7.9%.

Fraction 2, identified as 4-hydroxy-isobutyrophenone, distilled as an oil (2.2 gm., 11%) boiling at 128°C. (0.1 mm.). On standing the oil solidified and recrystallization from ether – petroleum ether gave the pure compound m.p. 54°C. Literature (8), m.p. 56°C. *2,4-Dinitrophenylhydrazone*, m.p. 166°C. (decomp.). Anal. calc. for $C_{16}H_{16}O_5N_4$: N, 16.2%. Found: N, 16.2%. *Semicarbazone*, m.p. 199°C. Anal. calc. for $C_{11}H_{15}O_2N_3$: N, 19.0%. Found: N, 19.1%. *Oxime*, m.p. 159°C. Anal. calc. for $C_{10}H_{13}O_2N$: N, 7.8%. Found: N, 7.7%.

Low Temperature Fries Rearrangement of Phenyl Isobutyrate

Phenyl isobutyrate (11 gm., 0.07 mole) was added in small portions at room temperature to a solution of anhydrous aluminum chloride (11 gm., 0.09 mole) in nitrobenzene (50 ml.). The reaction was allowed to proceed at 25°C. for 40 hr. and then the solution was poured on to ice and hydrochloric acid. When hydrolysis was complete the mixture was extracted with ether and the ethereal solution extracted with potassium hydroxide solution (1 *N*). The alkaline solution was acidified and re-extracted with ether. Removal of the solvent and distillation *in vacuo* yielded 4-hydroxy-isobutyrophenone (9.5 gm., 86%) boiling at 133°C. (0.5 mm.) and m.p. 54°C. on recrystallization from ether – petroleum ether (1).

The following crystalline derivatives were found not to depress the melting point of the same derivatives obtained from fraction 2 obtained in the high temperature rearrangement: 2,4-dinitrophenylhydrazone, m.p. 166°C. (decomp.); oxime, m.p. 159°C.; semicarbazone, m.p. 199°C.

Acylation of Phenol with Isobutyryl Chloride

Anhydrous aluminum chloride (13.3 gm., 0.1 mole) and a solution of phenol (4.7 gm., 0.05 mole) in nitrobenzene (50 ml.) were placed in a flask fitted with a mechanical stirrer and a reflux condenser. Isobutyryl chloride (5.3 gm., 0.05 mole) was gradually added with vigorous stirring and the solution heated on the steam cone for one half-hour with continuous stirring. The cooled solution was poured on to cracked ice and hydrochloric acid. Distillation of the resulting oil yielded two fractions which were separately redistilled.

Fraction 1 was identified as 2-hydroxy-isobutyrophenone (0.5 gm., 7%) which distilled as an oil boiling at 67°C. (0.7 mm.) and having n^{25}, 1.5355. 2,4-Dinitrophenylhydrazone m.p. 186°C. (decomp.).

Fraction 2 was identified as 4-hydroxy-isobutyrophenone (6 gm., 73%), which distilled at 135°C. (0.7 mm.) and on recrystallization melted at 54°C. 2,4-Dinitrophenylhydrazone m.p. 166°C. (decomp.).

2- and 4-Methoxy-isobutyrophenone

Dimethyl sulphate (3.2 gm.) was added to a solution of 2-hydroxy-isobutyrophenone (2.5 gm.) in water (50 ml.) containing potassium hydroxide (1.2 gm.). The solution was warmed to 50°C. and stirred for six hours. The oil which

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separated was extracted with ether and the ethereal solution was washed with aqueous alkali and with water. Removal of the ether and distillation yielded *2-methoxy-isobutyrophenone* (2.2 gm., 90%) boiling at 71°C. (0.3 mm.) and n^{25}, 1.5229. The oil showed no tendency to crystallize. Literature (13), m.p. 97–98°C. *2,4-Dinitrophenylhydrazone*, m.p. 136°C. Anal. calc. for $C_{17}H_{18}O_5N_4$: N, 15.6%. Found: N, 15.7%. *Oxime*, m.p. 105°C. Anal. calc. for $C_{11}H_{15}O_2N$: N, 7.2%. Found: N, 7.2%.

4-Methoxy-isobutyrophenone, prepared in a similar way, was obtained in 90% yield as an oil, b.p. 89°C. (0.3 mm.) and n^{25}, 1.5340. Literature, b.p. 82.7°C. (0.01 mm.) (11), n^{20}, 1.5363 (12). 2,4-*Dinitrophenylhydrazone*, m.p. 117°C. Anal. calc. for $C_{17}H_{18}O_5N_4$: N, 15.6%. Found: N, 15.6%. Semicarbazone, m.p. 181°C. Literature (11), m.p. 183–184°C. Anal. calc. for $C_{12}H_{17}O_2N_3$: N, 17.9%. Found: N, 17.9%. *Oxime*, m.p. 86°C. Literature (12) quotes the oxime as an oil. Anal. calc. for $C_{11}H_{15}O_2N$: N, 7.2%. Found: N, 7.2%.

Preparation of 2-Methoxybenzoic Acid and Anisic Acid

2-Methoxy-isobutyrophenone (2.0 gm., 0.01 mole) was added to a solution of anhydrous sodium carbonate (1.5 gm., 0.014 mole) and potassium permanganate (3.2 gm., 0.02 mole) in water (60 ml.) and the solution refluxed until oily drops were no longer observed in the condenser (about four hours). The cooled solution was filtered from precipitated manganese dioxide, the filtrate acidified with hydrochloric acid and extracted with ether. The ethereal solution was washed with water, dried with magnesium sulphate, and evaporated. The resulting solid, recrystallized from carbon tetrachloride, had m.p. 100°C. alone or when mixed with an authentic sample of 2-methoxybenzoic acid.

4-Methoxy-isobutyrophenone was oxidized in a similar manner and the acid obtained, recrystallized from water, had m.p. 184°C. alone or when mixed with an authentic sample of anisic acid.

Acylation of Anisole with Isobutyryl Chloride

Isobutyryl chloride (20 gm., 0.18 mole) was added with stirring over one half-hour to a mixture of anhydrous aluminum chloride (33 gm., 0.25 mole) and anisole (21 gm., 0.18 mole) in carbon disulphide (200 ml.). The solution was refluxed for one hour with stirring. The cooled reaction mixture was poured onto ice and hydrochloric acid and the aqueous layer extracted with ether. The oil resulting from the evaporation of the combined solvent extractions yielded two fractions on distillation and each was separately redistilled.

Fraction 1 gave 2-methoxy-isobutyrophenone (1 gm., 3%) as a liquid boiling at 75°C. (0.3 mm.) and having n^{25}, 1.5229. 2,4-Dinitrophenylhydrazone, m.p. 135°C.

Fraction 2 gave 4-methoxy-isobutyrophenone (19 gm., 60%) as a liquid boiling at 89°C. (0.3 mm.) and having n^{25}, 1.5341. 2,4-Dinitrophenylhydrazone, m.p. 115°C.

2-Isobutylphenol

2-Hydroxy-isobutyrophenone (2 gm.) was refluxed with a mixture of zinc amalgam (5 gm.), concentrated hydrochloric acid (8 ml.), and glacial acetic

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acid (8 ml.) until a negative test was obtained with 2,4-dinitrophenylhydrazine (about seven hours). 2-Isobutylphenol was obtained in 55% yield as an oil boiling at 62°C. (0.7 mm.). 3,5-Dinitrobenzoate m.p. and mixed m.p. 83°C. (6).

4-Isobutylphenol

4-Hydroxy-isobutyrophenone (2 gm.) was reduced as above and 4-isobutylphenol was obtained in 83% yield as an oil boiling at 82°C. (0.7 mm.). The oil solidified on standing and recrystallization gave the pure phenol m.p. and mixed m.p. 52°C. (1).

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POLYMER-ANALOGOUS DENITRATION OF POLYSACCHARIDE NITRATES: A STUDY OF SOME REDUCTIVE METHODS WITH MODEL COMPOUNDS AND CELLULOSE NITRATE[1]

By E. P. Swan[2] and L. D. Hayward

ABSTRACT

Crystalline D-mannitol penta- and hexa-nitrates, methyl-β-D-glucopyranoside tetranitrate, and maltose and cellobiose octanitrates were prepared as model substances of known constitution for study of denitration reactions possibly applicable to polysaccharide nitrates. Heterogeneous catalytic hydrogenation smoothly regenerated the parent carbohydrates from the model compounds in nearly quantitative yield and removed 0.42 and 0.63 nitrate groups per glucose unit from cellulose nitrates of 13.3 and 10.7% N respectively. Raney nickel was conveniently removed from the hydrogenated cellulose nitrates by means of a magnet. The action of methyl magnesium iodide, lithium aluminum hydride, or low-pressure hydrogenation with a homogeneous cupric acetate catalyst caused less complete denitration of the mannitol or cellobiose polynitrates. The nitration–fractionation–denitration sequence as a means of isolation of undegraded polysaccharides from natural sources is discussed.

INTRODUCTION

Nitration alone of all polysaccharide substitution reactions has been proved to be polymer-analogous* when carefully controlled (37, 23, 24, 25, 32). Nitration of plant tissue followed by fractionation (14, 25) with organic solvents has permitted separation of the nitrated polysaccharide components which, in the most careful work, were probably closely polymer-analogous to the "native" macromolecules (31); the physical properties of polysaccharide nitrate solutions thus obtained have been extensively studied, particularly for the commercial evaluation of cellulosic fibers of plant origin (8, 25).

So far the use of polysaccharide nitrate derivatives for chemical characterization of chain units and the sequence and branching patterns of the macromolecules has been limited by the lack of a method of quantitative and polymer-analogous denitration (5, 23, 28, 35). Such a method would complete the cycle of operations through which pure polysaccharides could be isolated from natural sources with minimum chemical alteration and in a form suitable for structural studies by conventional methylation, hydrolysis, and chromatography techniques.

The ease of quantitative removal of nitric acid ester groups with regeneration of the alcohol from alkyl and sugar nitrates by reported methods suggested that further study of these with certain hexitol, monosaccharide, and disaccharide polynitrates as model substances might lead to a method applicable to the nitrated polysaccharides. The model substances (Table I) were selected (*a*) to

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**We propose to define a polymer-analogous reaction as a chemical transformation of an organic polymer in which the carbon skeleton of the chains and units and the links between units remain unaltered.*

TABLE I

THE CARBOHYDRATE POLYNITRATE MODEL COMPOUNDS

Carbohydrate nitrate	Constants found				Reported constants				
	M.p.,°C.*	$[\alpha]_D^{20}$	*c*	Solvent	M.p.,°C.	$[\alpha]_D^{20}$	*c*	Solvent	Ref.
Cellobiose octanitrate	150	+88.92	5	Acetone	154 140	+22.18	6	Acetone	(2) (6)
Maltose octanitrate	164–165	+8.53	1	Dioxane	164–165 164–165	+128.6	35	Gl. HOAc	(2) (36)
D-Mannitol hexanitrate	111	+43.03	2	Ethanol	111–112	+43.1	2	Ethanol	(15)
D-Mannitol-1,2,3,5,6-pentanitrate	80	+47.16	4	Ethanol	81–82	+47.7	4.4	Ethanol	(7)
Methyl-β-D-glucopyranoside tetranitrate	115–116	+11.62	4	$CHCl_3$	116.5	+11.6	4	$CHCl_3$	(6)

**All melting points were corrected.*

contain atomic linkages characteristic of polysaccharides, (*b*) to yield on denitration easily identifiable parent compounds, and (*c*) to be preparable in crystalline form by direct nitration of the available parent substances. Their identity was established from the physical constants (Table I) and nitrogen analyses (Table IV) and by nearly quantitative denitration to the parent compounds (Table II).

Catalytic hydrogenation (15, 16, 19, 20, 21), hydrolysis of Grignard adducts (17), and reduction with lithium aluminum hydride (30) appeared to be the most promising methods of denitration and were selected for trial, while alkaline and acid hydrolyses and the solvolyses of nitric acid esters (1, 3, 4, 11, 12, 18, 22, 25) were rejected as unsuitable for polysaccharide structure studies.

The results obtained from the application of Kuhn's catalytic hydrogenation method (15, 19, 21) to the model carbohydrate nitrates are summarized in Table II. The yield of reasonably pure parent substance was excellent in each

TABLE II

PRODUCTS FROM HYDROGENOLYSIS OF THE MODEL COMPOUNDS*

Parent carbohydrate	Number of nitrate groups	Yield, %	M.p.,°C.†	Mixed m.p.,°C.†	Reported m.p.,°C.
β-Cellobiose	8	99.2	242	241	225 (26); 230 (34)
β-Maltose.H_2O	8	99.5	98–100	98–100	102–103 (26)
D-Mannitol	6	97.5	161–164	161–163	166 (26)
D-Mannitol	5	99.9	166–167	166–167	166 (26)
Methyl-β-D-glucopyranoside.$1/2H_2O$	4	99.5	104–107	104–106	104–106 (27)

**In ethanol at 25°C., hydrogen pressure 30–57 p.s.i., palladium–charcoal catalyst, 0.3 to 0.5 gm. per gram of nitrate.*

†All melting points were corrected.

case and the identity of the product was established by a mixed melting point with an authentic specimen.

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Hepworth (17) in 1921 reported that alkyl nitrates were denitrated by the action of methyl or ethyl magnesium halides followed by dilute acid hydrolysis of the Grignard adduct; the only product which had been isolated however was N,N-dimethyl (or ethyl) hydroxylamine. When applied by us to D-mannitol hexanitrate and cellobiose octanitrate this procedure gave 34 and 11% yields respectively of the corresponding polyols isolated as the fully acetylated derivatives. To avoid degradation the Grignard addition complex was broken up with dilute acetic acid, and concentration and acetylation of the residue were necessary to separate the water soluble polyols from the inorganic salts.

Reduction of D-mannitol hexanitrate by an ethereal solution of lithium aluminum hydride (30) gave an 87% yield of D-mannitol isolated as the corresponding hexaacetate. The adverse side reactions anticipated from the formation of ammonia and nitrous oxide, the degradative action reported by Soffer *et al.*, and the necessary acetylation step weighed against the general usefulness of this reaction as a denitration technique for the more sensitive sugar and polysaccharide polynitrates.

Two problems were encountered in applying the catalytic hydrogenation method to cellulose nitrate: (*a*) the reaction stopped when the partially denitrated product became sufficiently insoluble in the hydrogenation solvent to form a fourth phase, and (*b*) the removal of the heterogeneous catalyst from the product was difficult. Since the problems could not be solved by selection of a solvent mixture compatible to both nitrated and denitrated forms, it was first considered that the use of a homogeneous hydrogenation catalyst might outweigh the adverse effect of the formation of a solid phase in the reaction and also permit separation from the denitrated polymer.

Cupric or cuprous acetate was used in pyridine solution by Calvin (10) and by Weller and Mills (33) to catalyze the reduction of quinone to hydroquinone. Although pyridine caused extensive decomposition of cellulose nitrate (13, 29), the pentanitrates of mannitol and dulcitol were stable to the base at room temperature (15, 21). D-Mannitol-1,2,3,5,6-pentanitrate in a homogeneously catalyzed hydrogenation in pyridine with cupric acetate consumed a small and

TABLE III

ANALYSES OF CELLULOSE NITRATE SAMPLES

Cellullose nitrate	% N	% Ash	D.S.*	M†	Method of preparation
A	13.37, 13.24	0.162	2.72	285	100% $HNO_3+P_2O_5$(29)
B	12.11, 12.15	0.075	2.30	265	Hydrogenolysis of A
C	10.72, 10.65‡	0.162	1.88	247	N_2O_5 in $CHCl_3$ (9, 32)
D	2.73, 2.77	2.1	1.25§	218§	Hydrogenolysis of C
E	12.40, 12.54	0.053			

Degree of substitution $= \frac{3.60 \times \% \text{ N}}{31.13 - \% \text{ N}}$ (24).

†*The submolecular weight of the nitrated pyranose residue* $= \frac{5046}{31.13 - \% \text{ N}}$ (24).

‡*By semimicro nitrometer, other* N *values by modified micro-Kjeldahl method* (29).

§*Calculated for the total product,* D *plus* E.

uncertain amount of hydrogen and was not completely denitrated. The only crystalline organic product isolated appeared to be a copper salt of a strong organic acid and was not investigated further.

In a second attack on problem (*b*), cellulose nitrate samples A and C (Table III) were hydrogenated over Raney nickel catalyst, the nickel being removed from the hydrogenated mixture at the end of the reaction by means of a magnet. Cellulose nitrate A gave a fibrous product, cellulose nitrate B, in 82% yield based on the nitrate–nitrogen analysis. The ash content of B was negligible and the D.S. value of 2.30 indicated that denitration had been achieved to the extent of 0.42 nitrate groups per pyranose unit. Cellulose nitrate C under similar conditions gave a suspension of cellulose nitrate D in a solution of a more highly substituted cellulose nitrate E. The D.S. value of the total product (D plus E) again indicated a substantial denitration of 0.63 nitrate groups per glucose unit and the improved total yield of 98% (based on the analyses) could be attributed to the lower solubility and hence better recovery of the less highly substituted product.

It was concluded that the hydrogenation method holds promise for achieving complete polymer-analogous denitration of polysaccharide nitrates and warrants further study.

EXPERIMENTAL

Materials and Methods

The usual precautions (16, 21, 29) were observed in handling the high explosive nitrated compounds.

Cellobiose octaacetate was prepared from cotton wool and deacetylated in 82% yield to give pure cellobiose after four recrystallizations from aqueous methanol; m.p. 242°C., $[\alpha]_D^{20}$ from +22.29 to +34.45° (*c*, 4; water); the previously reported constants are shown in Table II. Nitration of cellobiose and of maltose with nitric–sulphuric acids (36) at 0°C. gave the crystalline octanitrates (Tables I and IV) in 64 and 40% yields respectively after purification

TABLE IV

NITROGEN ANALYSES OF MODEL COMPOUNDS

Carbohydrate nitrate	Found, % N	Calc., % N	Method*
Cellobiose octanitrate	15.78, 15.82	15.92	(*a*)
Maltose octanitrate	15.72, 16.46	15.92	(*b*)
D-Mannitol hexanitrate	18.30, 18.57	18.55	(*a*)
D-Mannitol-1,2,3,5,6-pentanitrate	17.28, 16.79	17.23	(*a*)
Methyl-β-D-gluco-pyranoside tetranitrate	14.53, 14.59	14.56	(*b*)

*(*a*) = *Semimicro Dupont nitrometer* (*29*).
(*b*) = *Modified micro-Kjeldahl* (*29*).

by the method of Ashford *et al.* (2) with care to keep the temperature below 30°C. during evaporation. The other model compounds were prepared as previously described (7, 15, 16).

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Absorbent cotton was extracted in a Soxhlet apparatus for successive two-day periods with 1:2 ethanol–benzene and then with ligroin and dried for one month at 56°C. *in vacuo* over phosphorus pentoxide. One half to one gram samples of the bone-dry cellulose (copper number 0.247) were nitrated in 92 to 100% yield (based on nitrogen analyses) as noted in Table III. The nitrates were washed free of acids with 50% ethanol at −10°C., stabilized by refluxing with ethanol (29), and dried *in vacuo*; the analyses are reported in Table III.

The catalytic hydrogenation of the model compounds (Table II) confirmed their identity and followed the procedure described in earlier publications (15, 16, 20).

Reduction with Grignard's Reagent

D-Mannitol hexanitrate (0.93 gm.) dissolved in anhydrous tetrahydrofuran (20 ml.) was added to a cold solution of methyl magnesium iodide prepared in 50 ml. of anhydrous ether from 6.6 gm. of methyl iodide and 1.13 gm. of magnesium turnings (17). After 24 hr. at room temperature the reaction mixture was treated with water (50 ml.) and glacial acetic acid (5 ml.) and extracted with ether. Evaporation of the ether extract left a yellow sirup (0.21 gm.) which gave a positive diphenylamine test. The aqueous solution was evaporated under reduced pressure and the solid residue was acetylated at room temperature with pyridine (25 ml.) and acetic anhydride (25 ml.). Free iodine was liberated in an exothermic reaction on contact of the residue with these reagents and was removed by treatment with 10% sodium thiosulphate solution after the acetylation mixture had been diluted with ice water. Extraction of the aqueous mixture with chloroform and evaporation of the dried chloroform solution yielded crystalline D-mannitol hexaacetate (0.30 gm.) which melted at 114–116°C. after two recrystallizations from aqueous ethanol; a mixed melting point with authentic D-mannitol hexaacetate was 113–116°C.

Cellobiose octanitrate (0.95 gm.) when treated with the Grignard reagent in a similar manner yielded an ether-soluble, partially nitrated sirup (0.17 gm.) and crystalline cellobiose octaacetate (0.10 gm.) melting at 207–214°C.; the mixed melting point with authentic cellobiose octaacetate (m.p. 229.5°C.) was 219°C.

Reduction with Lithium Aluminum Hydride

Twenty milliliters of a solution of lithium aluminum hydride in ether (98.3 gm. per liter) was stirred magnetically in a two-necked flask fitted by ground glass joints with a reflux condenser and a dropping funnel. A slow stream of nitrogen was passed continuously over the solution while D-mannitol hexanitrate (0.95 gm.) in dioxane (20 ml.) was admitted dropwise through the funnel and the exothermic reaction was controlled by external cooling. After the addition was complete the mixture was stirred for a further three hours at 0°C. and then refluxed for one half hour. At the end of this time ethyl acetate (10 ml.) was added to decompose any remaining hydride, and this was followed by the addition of wet ether and then water. Separation and evaporation of

the ether layer yielded a brown sirup (0.05 gm.) which gave a positive diphenylamine test. Acetic acid (10 ml.) was added to the aqueous solution which was then evaporated. The solid residue was acetylated and worked up with chloroform to give a pale yellow sirup (0.79 gm.) which crystallized on standing. After recrystallization from aqueous ethanol the product melted at 119°C. and did not depress the m.p. of D-mannitol hexaacetate. The yield of D-mannitol from the denitration reaction amounted to 87% of the theoretical value.

Reduction with Hydrogen and Cupric Acetate in Pyridine

D-Mannitol-1,2,3,5,6-pentanitrate (0.97 gm.) and cupric acetate (0.44 gm.) were dissolved in pyridine (100 ml.) and the solution was shaken with hydrogen at room temperature and 55 p.s.i. for 24 hr. At the end of this time, blue, water-soluble crystals were observed on the walls of the reaction vessel and were washed into the pyridine solution, which was then evaporated to dryness under reduced pressure. The residue was taken up in water, and the aqueous solution was freed of copper by treatment with hydrogen sulphide and then extracted with ether. Evaporation of the ether solution left a brown, nitrate-containing sirup (0.27 gm.) and evaporation of the aqueous layer gave a crystalline product (0.32 gm.) which melted at 75–91°C., caused the evolution of carbon dioxide from sodium bicarbonate solution, and gave a positive diphenylamine test. An aqueous solution of the crystalline material was acid to Congo red.

In blank runs cupric acetate and mannitol pentanitrate, separately dissolved in pyridine, consumed no hydrogen at 25°C. and 55 p.s.i. during 24 hr.

Reduction of the Cellulose Nitrates

Cellulose nitrate A (Table III) (0.53 gm.) dissolved in ethylene glycol monomethyl ether (50 ml.) was hydrogenated for 46 hr. at 56 p.s.i. with Raney nickel catalyst. The product was a black suspension to which was added acetone (150 ml.) and the mixture was stirred for an hour over a magnet (field strength 4845 gauss) which attracted the nickel to the bottom of the reaction vessel. The clear supernatant liquid was decanted from the catalyst while the bottom of the vessel remained in contact with the magnet and the nickel was washed three times with acetone by this procedure. The washings were added to the original solution which was then poured with stirring into cold water (1 liter). The precipitated cellulose nitrate was recovered on a glass filter and washed with cold water, pressed, and then dried *in vacuo* for three days over phosphorus pentoxide. The mass of dry, coarse, white fibers (0.40 gm.) was analyzed for ash and nitrogen (cellulose nitrate B, Table III).

Cellulose nitrate C (0.66 gm.) was hydrogenated by the above procedure for 24 hr. and after separation of the catalyst the product appeared as a suspension of cellulose nitrate in a solution of a more highly substituted cellulose nitrate. The suspended fibers (cellulose nitrate D) were recovered by centrifugation, washed with acetone, dried (yield 0.26 gm.), and analyzed (Table III). The combined centrifugate and washings were worked up as described for cellulose nitrate C and the white fibrous product (0.31 gm.) was similarly dried and analyzed (cellulose nitrate E).

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REACTIONS OF ARYLSULPHONIC ESTERS

IV. AN INTERPRETATION OF SOLVOLYTIC ACTIVATION ENERGIES[1]

By J. B. Hyne[2] and R. E. Robertson

ABSTRACT

A semiempirical equation is presented relating the activation energies of some fifty solvolyses of benzenesulphonic esters to physical properties of the solvolyzing medium. The equation predicts more than 70% of these activation energies to better than 300 cal./gm-mol. The significance of the equation is discussed on the basis of a continuous spectrum of mechanisms intermediate between the accepted S_N1 and S_N2 types. A suggested interpretation of the log PZ (activation entropy) term is also offered.

INTRODUCTION

The postwar years have seen marked advances in the theory of the mechanism of solvolytic reactions. Stemming largely from the S_N1, S_N2 mechanistic classification of Hughes, Ingold, and co-workers (19) development and modification of the original hypothesis has led to significant advances in this field of reaction kinetics. Further development has been based upon a free energy interpretation of solvolytic reactions, foremost in this field being Hughes, Ingold, and co-workers (8), Grunwald and Winstein (12, 13), Swain and co-workers (30, 31), Hudson and co-workers (2, 4), and Tommila and co-workers (33, 34, 35). Particular note, however, must be taken of the work of Moelwyn-Hughes *et al.* (9, 23, 24, 25) whose efforts in this field have been directed toward an interpretation of the temperature dependence of solvolytic rates of reaction.

In recent years, there has been a growing interest in the possibility that the accepted S_N1 and S_N2 mechanisms may only be the limiting cases in a continuously varying range of mechanisms. Unambiguous evidence of such behavior is difficult to obtain but many workers have found indications that such a situation does exist (see Theoretical, 2). Doering and Zeiss (6) have outlined in considerable detail the energetics of such intermediate mechanisms. Gold (10), on the other hand, has presented evidence which is claimed to be inconsistent with a unique intermediate mechanism.

We have interpreted the activation energies of the solvolyses of benzenesulphonic esters in hydroxylic solvents upon the principle of a continuous spectrum of intermediate mechanisms varying between the two limits of S_N1 and S_N2. The principle of such "hybrid" mechanisms must, of necessity, be open to critical argument but we feel that there is sufficient significance in the point of view to be presented to warrant its consideration as a development in the general theory of solvolytic reaction mechanisms.

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RESULTS

In Table I are collected the activation energies interpreted in this paper. These values have been recalculated from the original rate data and in some cases differ by a few per cent from the values given in the origin reference. The bulk of the work was carried out in this laboratory although in one or two

TABLE I

SOLVOLYTIC ACTIVATION ENERGIES, LOG PZ FACTORS, AND α VALUES

1 Ester*	2 Solvent	3 α	4 E_a(obs.), cal./gm-mol.	5 E_a(calc.), cal./gm-mol.	6 ΔE_a	7 t_m,°C.	8 logPZ_{obs}	9 Ref.
Me-*p*H	H_2O	0	20520	20470	50	62	10.181	22
	MeOH		20973	21264	−291	60	9.317	26
	EtOH		20400	20354	46	80	8.847	22
	*i*PrOH		19150	19414	−264	63	7.870	18
Me-*p*Me	H_2O	15	21038	21192	−154	62	10.369	27
	MeOH		21390	21987	−597	50	9.494	26
	EtOH		20944	21076	−132	66	8.988	26
	*n*PrOH		20882	20161	721	66	8.863	28
	*i*PrOH		19500	20137	−637	74	7.806	28
	*n*BuOH		19415	19144	271	80	7.896	28
	*i*BuOH		18559	19029	−470	80	7.259	28
	*s*BuOH		17964	19238	−1274	80	6.662	28
	*i*AmOH		18593	18085	508	90	7.314	28
	β-PhEtOH		18243	17454	789	90	6.813	28
Et-*p*H	H_2O	19	21040	21384	−344	62	10.500	22
	MeOH		22180	22179	1	70	9.819	26
	EtOH		21380	21269	111	80	9.107	22
Et-*p*Me	H_2O	34	21581	22007	−426	62	10.699	29
	MeOH		22800	22902	−102	67	9.925	26
	EtOH		21980	21991	−11	67	9.208	26
	*i*PrOH		21400	21076	324	68	8.470	28
*i*Pr-*p*H	H_2O	42	22659	22492	167	17	13.424	22
	MeOH		23000	23287	−287		11.130	35
	EtOH		22950	22377	573	60	10.627	22
	*i*PrOH		21630	21437	193		9.252	35
*i*Pr-*p*Me	EtOH	55	22900	23003	−103	65	10.400	26
*n*Pr-*p*H	H_2O	26	21500	21722	−222	62	10.520	22
	EtOH		21669	21606	63	73	9.050	22
*n*Bu-*p*H	H_2O	10	20530	20951	−421	50	10.040	22
	EtOH		20941	20835	105	90	8.587	22
*i*Bu-*p*H	H_2O	63	23494	23504	−10	73	11.483	22
	EtOH		23212	23388	−166	73	8.949	22
*n*Pen-*p*H	H_2O	11	20700	20999	−299	50	10.173	22
	EtOH		21082	20883	199	87	8.712	22
Me-*p*Br	MeOH	7	21150	21601	−451	57	9.863	26
	EtOH		20773	20691	82	56	9.420	26
	*i*PrOH		19797	19751	46	61	8.600	28
Et-*p*Br	EtOH	26	21596	21606	−10	61	9.410	26
*i*Pr-*p*Br	MeOH	47	23200	23528	−328	47	11.522	26
	EtOH		22330	22618	−288	65	10.652	26
	*i*PrOH		21600	21578	22	62	9.700	28
Me-*p*NO_2	EtOH	9	20730	20787	−57	55	10.000	26
Et-*p*NO_2	EtOH	29	21680	21750	−70	57	10.247	26
*i*Pr-*p*NO_2	EtOH	50	22880	22762	118	60	11.661	26
Me-*m*NO_2	EtOH	6	20690	20643	47	55	10.062	26
Et-*m*NO_2	EtOH	24	21338	21510	−172	57	10.104	28
Me-*p*F	H_2O	13	21027	21095	−68	60	10.581	28
Me-*p*MeO	H_2O	20	21500	21433	67	55	10.375	28
	EtOH		21080	21317	−237	80	8.927	26
Et-*p*MeO	EtOH	36	21848	22088	−240	80	9.071	26

**Method of notation of esters will be obvious from the following: Me-pH = methyl benzenesulphonate; Me-pMe = methyl p-methyl benzenesulphonate.*

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cases results of Tommila and co-workers are used. In the majority of cases where comparison is possible agreement with other work is good. No experimental details are given since these have been previously presented with the rate data in the origin references.

Table I shows for each ester (column 1) in each solvent (column 2) an observed (column 4) and calculated (column 5) activation energy and the difference between the two values (column 6). The observed log PZ term (column 8) is also recorded. Column 3 records an α value, characteristic of the ester, the physical significance of which is discussed later. The mean of the temperatures at which the individual rate determinations were made is shown in column 7. In those cases where this mean is considerably different from the average value the possibility of error due to neglect of temperature dependence of activation energy must be considered (see section—Interpretation of Activation Energies). In the majority of cases the observed activation energy may be quoted to better than ±200 cal./gm-mol. Column 9 gives the origin reference. The dielectric constants and molecular volumes of solvents used in the evaluation of the calculated activation energy are shown in Table II. The dielectric constant at 20°C. was employed as this was the most convenient temperature for obtaining data for the less common solvents. As the D value is used only as a measure of relative solvent dielectric strength, this introduces no serious error.

TABLE II

DIELECTRIC CONSTANTS AND MOLECULAR VOLUMES OF SOLVENTS

Solvent	D	t, °C.	Ref.	MV
H_2O	80.4	20	(1)	18
MeOH	32.4	20	(1)	40
EtOH	25.0	20	(1)	58.4
*n*PrOH	20.8	20	(1)	74.6
*i*PrOH	18.6	20	(1)	76.5
*n*BuOH	17.8	25	(20)	91.5
*i*BuOH	18.7	20	(20)	92.5
*s*BuOH	15.5	19	(20)	91.7
*i*AmOH	15.3	23	(20)	108.6
β-PhEtOH (value for benzyl alcohol)	13.0	20	(11)	119.4

THEORETICAL

1. *Nucleophilic Substitution Mechanisms*

The S_N1 and S_N2 mechanisms introduced by Ingold and Hughes (14, 15, 16) are now widely accepted as a firm base on which further work on the mechanism of nucleophilic substitution reactions may be developed. A brief resume of the principles involved in these mechanisms is of value here. S_N1 takes place through the formation of an intermediate ionic state, the ions being stabilized by solvation. Formation of the ionic intermediate is the rate

$$A - B \xrightarrow[slow]{} [\text{Transition State}] \rightarrow \underset{\text{Intermediate}}{[A^+ + B^-]} \xrightarrow[fast]{C} [\text{Transition State}] \rightarrow \text{Product}$$

determining stage in the reaction. The rates and activation parameters measured are therefore associated with the formation of the first transition state. S_N2, in contrast to the S_N1 mechanism, is often referred to as a single

$$A - B + C \rightarrow \underset{\text{Transition State}}{[A- -B- - -C]} \rightarrow \text{Products}$$

stage reaction. The reactant AB does not undergo preliminary dissociation before reacting with component C; scission of the AB bond and formation of the CB bond take place simultaneously in the transition state.

Criteria for distinguishing between these mechanisms have been proposed and discussed by many workers (14). The failure of these criteria to establish the mechanism of certain reactions has led to the proposal by several workers of mechanisms intermediate between S_N1 and S_N2.

2. *Evidence for Intermediate Mechanisms*

Following upon the initial exploitation of the S_N1 and S_N2 mechanistic theory examples were found of reactions which exhibited phenomena typical of both S_N1 and S_N2 mechanisms. Bateman, Hughes, and Ingold (3) established a criterion for mechanism based upon the relationship of product ratio and rate in mixed solvolysis. In cases where such a relationship existed an S_N2 mechanism was found to explain the observed dependence and in the absence of any relationship, as for *tert*-butyl chloride in aqueous alcohol, an essentially S_N1 mechanism was proposed. The operative word here is "essentially" since there is only evidence for a charged intermediate in the *tert*-butyl chloride case, not for the separable ions of the pure S_N1 mechanism. The indications are, therefore, that although the mixed solvolysis of *tert*-butyl chloride does not conform to S_N2 mechanics, there is little evidence to support the conclusion that it proceeds by a pure S_N1 mechanism. Swain and Moseley (31) have illustrated this point by comparing the rates of solvolysis of triphenylmethylfluoride, *tert*-butyl chloride, and *n*-butyl bromide and showing that the mechanistic behavior of *tert*-butyl chloride is intermediate between that of triphenylmethylfluoride (S_N1) and *n*-butyl bromide (S_N2).

The influence of bulk dielectric constant of the medium upon reaction rate has also been employed as a criterion of mechanism. Since the formation of the ionic intermediate in the S_N1 case is more dependent upon dielectric of the medium than the covalent bond-making, bond-breaking process of the S_N2 mechanism, it is generally accepted that the rates of S_N1 reactions are more markedly affected by change in dielectric constant than those of S_N2 reactions (19). A clear-cut boundary between S_N1- and S_N2-type reactions would therefore be expected to lead to a similarly clear-cut grouping of reaction rates highly dependent on dielectric constant and those less markedly dependent. Such behavior has been observed by Cowan, McCabe, and Warner (5) for several solvolytic reactions plotting k vs. $(D-1)/(2D+1)$, but the group exhibiting the most marked dependence of rate on dielectric constant included *tert*-butyl chloride for which there is strong evidence of an intermediate type of mechanism. Archer and Hudson (2), in their work on the solvolysis of acid chlorides, have shown that the rate dependence on dielectric constant under-

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goes a marked increase as the aqueous content of the acetone/water solvent increases. These authors considered this behavior as evidence of a change of mechanism from S_N2 to S_N1 but there is no indication that the change is sudden. Rather do the data support the idea that the mechanism is continuously changing from an "S_N2-like" mechanism at low water content to an increasingly "S_N1-like" mechanism. Grunwald, Winstein, and Jones (13) have applied their correlation of solvolysis rates to the investigation of solvolytic systems belonging to the so-called "borderline" class of mechanisms and have shown that interpretation of rate behavior in terms of two different simultaneous processes is not possible. They conclude that there is a unique mechanism operative in these "borderline" cases. Brown and Hudson (4) also illustrated the well-established dependence of activation energy upon mechanistic type. In the solvolysis of benzoyl chloride, for example, the activation energy increases continuously as the ionizing power of the medium increases and the mechanism becomes more "S_N1-like".

Doering and Zeiss (6) provide stereochemical evidence for intermediate mechanistic behavior in their studies of the methanolysis of optically active hydrogen 2,4-dimethylhexyl-4-phthalate where solvolysis is accompanied by roughly 50% racemization and 50% inversion.

There is then no lack of evidence to suggest that the original S_N1, S_N2 mechanistic classification represents but the extreme limits of a whole range of possible intermediate mechanisms.

3. *S_N12 Intermediate Mechanisms*

As a tieback for the present work we make special reference to the paper of Doering and Zeiss (6). The idea of a complete range of mechanisms between the limiting cases of S_N1 and S_N2 involving an intermediate of varying stability has been clearly expounded by these authors. Henceforth, we shall refer to such intermediate mechanisms as S_N12. Our development of the intermediate mechanism, with a view to explaining the kinetics of benzenesulphonic ester solvolysis, is, in essence, similar to the Doering and Zeiss hypothesis although there are several differences in detail.

In the accepted S_N2 mechanism bond breaking in the ester molecule and covalent interaction of the ester with the solvent molecule occur simultaneously. If we envisage the covalent interaction entering progressively later in the reaction path, in the limit bond breaking in the ester molecule will proceed to completion with the formation of solvation stabilized ions before covalent interaction with the solvent takes place. This limiting case is in fact the condition characteristic of an S_N1 mechanism. The S_N12 spectrum of intermediate mechanisms occupies this range between S_N2 and S_N1 brought about by the increasing interval between commencement of bond breaking in the ester and onset of covalent interaction with the solvent. It is not unreasonable to assume, moreover, that a solvation stabilized intermediate will exist without the actual formation of ions. A solvation stabilized intermediate ester species may then be envisaged in which there is charge separation in the ester bond eventually to undergo scission. The stability of this intermediate will be greater the greater the charge separation, i.e. the more "S_N1-like" the S_N12

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mechanism becomes. As the S_N2 end of the S_N12 spectrum is approached, however, the onset of covalent interaction becomes progressively nearer to the onset of charge separation in the reaction path. A very unstable intermediate will then be formed and in that region of the spectrum of S_N12 mechanisms very close to the S_N2 type the intermediate may have no real stability. The position occupied on the S_N12 spectrum of mechanisms by the series of benzenesulphonic ester solvolyses studied in this work cannot be firmly established on the evidence available. We have assumed, however, that even in the most "S_N2-like" reaction mechanism, namely, the solvolysis of methyl benzenesulphonate, there is a real intermediate formed albeit of low stability. In discussing the application of the S_N12 mechanism to the solvolysis of benzenesulphonic esters, therefore, we have not considered that part of the S_N12 range near the S_N2 end where there is no actual existence of an intermediate.

In the S_N12 mechanism as applied to these solvolytic reactions the charge separated intermediate is reached through a transition state, the formation of which is the rate determining step in the S_N12 mechanism. The charge separated intermediate is stabilized through solvation by molecules of the solvolyzing

$$A - B \xrightarrow[slow]{} [\text{Transition State}] \rightarrow \underset{\text{solvated}}{[A^{\delta-}\cdots B^{\delta+}]} \xrightarrow[fast]{C} \underset{\text{Transition State}}{[A\cdots B\cdots C]} \rightarrow \text{Products}$$

medium and the extent of charge separation in the intermediate is the determining factor in placing the mechanism in its relative position in the range between the limiting S_N1 and S_N2 cases. Since all observed rates and derived activation parameters provide information only on the rate determining stage, the mechanism of the subsequent reaction of the intermediate with C to give products cannot be supported, at this stage, by experimental facts. We can say, however, that during this second activation process one of the molecules involved in the solvation of the intermediate must become covalently bonded to the intermediate to form the second transition state. In a subsequent paper (18) we deal with the interpretation of the solvolysis of benzenesulphonic esters in *mixed* solvents where the question of the detailed nature of the solvation and the second transition state is more fully discussed.

In the present picture the distance along the reaction parameter r (Fig. 1) at which covalent interaction becomes important determines the relative position of the first transition state (T_{cs} = charge separated transition state) with respect to the second transition state (T_c = covalent transition state). When the two transition states are coincident the mechanism is S_N2 with no intermediate (curve (1), Fig. 1). As covalent interaction between solvent and reacting solute enters further along the reaction parameter r, a solvation stabilized intermediate will appear, the stability of the intermediate increasing as the point of entry of covalent interaction is further removed from the charge separated transition state. This whole range of varying stability of intermediates of increasingly greater charge separation represents the spectrum of S_N12 mechanistic types. One such S_N12 mechanism is depicted in Fig. 1,

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curve (2). Eventually, covalent interaction enters so far along the reaction parameter r that the charge separation in the intermediate proceeds to complete ionization with solvation stabilization of the ions and the mechanism becomes limiting S_N1 (Fig. 1, curve (3)). The relative heights of the first maxima in the three curves of Fig. 1 are without significance as drawn. This point is considered in greater detail in Fig. 6 with specific cases from the benzenesulphonic ester solvolyses. It will be noted from Fig. 1, however, that the second, or covalent transition state, T_c, is at a lower energy level than the first, or charge separated transition state, T_{cs}, in each curve since the attainment of the first transition state is the rate determining process. Further, the height of the second energy barrier approaches that of the first as the mechanism moves through the S_N12 range from S_N1 to S_N2 until the two transition states become one in S_N2. This is in keeping with the picture of *decreasing* charge separation in the intermediate on moving from S_N1 to S_N2 since it will require greater activation energy to bring about covalent interaction between the decreasing charge separated intermediate and the dipolar solvent molecule.

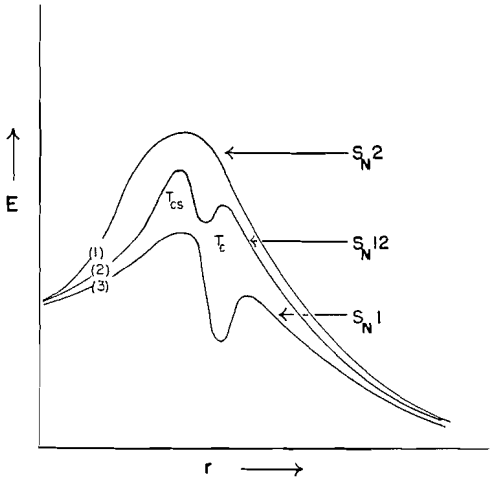

FIG. 1.

INTERPRETATION OF ACTIVATION ENERGIES

1. *Aim*

In the tables of results previously presented we have collected the experimentally determined activation energies of some fifty solvolytic reactions of benzenesulphonic esters. On the basis of the S_N12 mechanism outlined in the foregoing section we have established an equation from which these activation energies may be calculated with a precision well within the experimental error associated with the determinations. Previously published work from this laboratory (17, 27) has shown that the temperature dependence of the activation energy of such solvolytic reactions is significant and the fact that this dependence has not been taken into account in this study must be borne in mind. The

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determination of the temperature dependence of the activation energies used in this correlation is now in progress in this laboratory but in view of the lengthy nature of this work it is unrealistic to assume that neglect of this factor seriously detracts from the value of presenting the treatment in its present form. Furthermore, the agreement between observed and calculated values of the activation energies is such as to suggest that any error introduced through neglect of the temperature dependence is minimized by the particular set of conditions obtaining in the series of activation energies presented. Those few cases where agreement is poor may be due to neglect of this factor.

2. *Components of the Activation Energy*

The observed activation energy of the S_N12 mechanism is, by definition, associated only with the first, charge separated, transition state. Consider the factors which would be expected to lead to the difference in energy between the initial and transition states. Any component of the over-all activation energy resulting from covalent interaction between ester and solvent molecules in the initial rate determining transition state will be negligible as a result of the assumed position of the range of these solvolytic mechanisms on the S_N12 spectrum; that is, covalent interaction in the initial transition state is very small. Energy, however, will be required to bring about charge separation in the ester bond eventually to undergo scission; this component of the activation energy we denote as E_e. That the initial state of the system involves solvation of the ester cannot be denied; the charge separation created in the transition state, however, will result in greater attractive force being exerted by the ester molecule on the solvent molecules leading to an increase in extent of solvation in the transition state. *To a first approximation* the nature of solvation of the ester molecule at points other than around the seat of reaction ($-SO_3$ group) may be assumed to be the same in the initial and transition states so that the difference in extent of solvation will be largely centered on the SO_3 group. Solvent molecules, therefore, must be removed from the solvent lattice to be available for their solvating role. This component of the activation energy we denote as E_s. We now have $E_a = E_e + E_s$. The two components of E_a must now be related to some measurable parameters of the system in order to obtain an expression for E_a. Consider firstly E_e—the energy required for charge separation in the reactive bond. For any given ester this must be related to the dielectric constant of the surrounding medium. We at once recognize that the bulk dielectric constant of the solvent medium is not truly representative of the localized dielectric in the immediate vicinity of the created partial charges. Some measure of success has previously been achieved with relations involving the bulk dielectric constant, however, and in the absence of a better measure of dielectric of the medium we employ the bulk dielectric constant, bearing in mind this possible source of error. We then have $E_e = f(D)$. The solvation energy component E_s does not lend itself to such simple interpretation as E_e. The number of solvent molecules which can be accommodated in the first solvation shell (that largely determining E_s) must be a function of the molecular volume of the solvent species. The increased solvation of the transition state requires rupture of solvent–solvent bonds in the solvent lattice to free the molecules for their solvating role. We now make the assump-

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tion, again bearing in mind a possible source of error, that in the hydroxylic solvents all solvent–solvent hydrogen bonds, being of the O—H- - -O type, are of the same energetic magnitude. Therefore the increase in number of solvent molecules in the solvation shell of the transition state will be a relative measure of the solvation energy which, in turn, must be related to the molecular volume of the solvent species; let this be an $E_s = f(MV)_s$ proportionality. E_a may then be expressed as $E_a = f(D) + f(MV)_s$. We must now attempt to find the nature of these functions. It is not denied that the form of the functions may be derivable on a theoretical basis. Since, however, we are primarily interested in establishing only a quantitative expression for E_a we have adopted an empirical approach.

It is noted that the E_a's for the solvolysis of methyl benzenesulphonate in water and in ethanol are almost the same. If $f(D)$ and $f(MV)_s$ are to be the only variables in the equation, then their relative values must be adjusted by constant multipliers such that the E_a's for these two solvolytic reactions are the same. This empirical approach led to the derivation of a constant multiplier for the $(MV)_s$ term = 1.43, and E_a for the methyl benzenesulphonate solvolysis in several solvents was plotted against $(D+1.43(MV)_s)$. A straight line equation of the form

$$E_a = a(D+1.43(MV)_s)+b \qquad [1]$$

was obtained where $a = -48.17$ and $b = 25{,}580$.

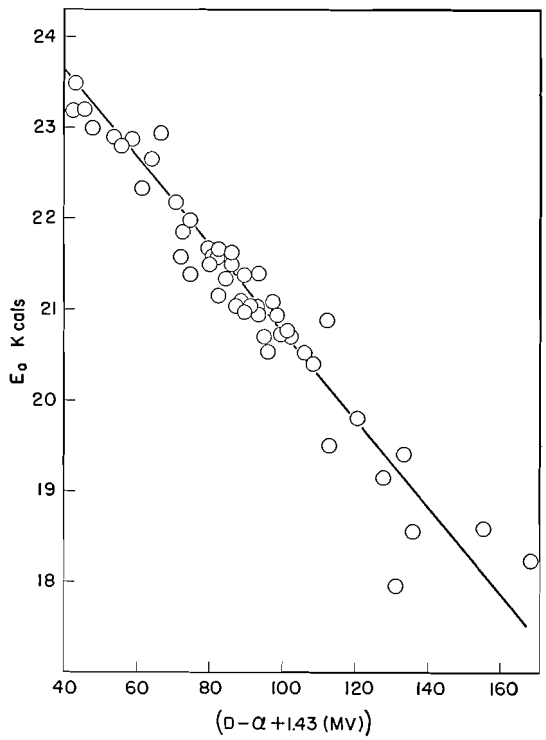

FIG. 2.

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3. *The α Value—Measure of Charge Separation*

On plotting the available activation energy data (Table I) against ($D+1.43(MV)_s$) it was found that for each ester a straight line was obtained in accordance with equation [1]. The lines were all of the same slope but displaced along the ($D+1.43(MV)_s$) axis. This was not surprising considering that when the relationship between E_s and D was discussed no account was taken of the variation of the ester species. The energy required to bring about charge separation in the transition state must be, to a considerable extent, dependent upon the groups on the reactive center of the ester. Such an effect cannot be measured by D since this is purely a property of the solvent medium. There is, of course, the possibility that the solvation energy, E_s, may vary with the extent of charge separation in the ester. We feel, however, that the important controlling factor in solvation is the molecular volume since in the range of compounds studied the difference in charge separation may not be too great and the size of the solvating species dominates the solvation effect.

A constant correction factor, α, for each ester was applied to the D value such that the plot of E_a vs. ($D-\alpha+1.43(MV)_s$) became coincident with the methyl benzenesulphonate line. The equation

$$[2] \qquad E_a = -48.17(D-\alpha+1.43(MV)_s)+25{,}580$$

was found to predict some 70% of fifty E_a's to better than 300 cal. This accuracy of prediction is comparable with the experimental error in E_a's for the majority of the reactions. The E_a's vary over some 6000 cal.

Undoubtedly the most interesting features of this correlation are the resultant α values. On the basis of the present theory (we suggest) they represent the relative magnitude of the charge separation in the transition states of the esters studied, based on the arbitrary zero of methyl benzenesulphonate. This does not mean, of course, that there is no charge separation in methyl benzenesulphonate. The α values derived are collected in Table III.

The effect on the α value of changing the complexity of the ester alkyl group (R) is clearly seen in Fig. 3. This effect appears to be independent of the *p*-group on the benzene ring as is manifest in the parallelism of the lines for esters with varying *p*-groups. The series methyl benzenesulphonate to *n*-pentyl benzenesulphonate (Table III(*a*)) plotted in Fig. 4 shows an increase in α to *n*-propyl benzenesulphonate beyond which the value decreases to a constant value. This behavior is somewhat similar to that observed by Everett, Landsman, and Pinsent (7) for the free energy and entropy of ionization of a series of fatty acids. This they attribute to chain stiffening in the longer hydrocarbon groups. Such an explanation may well be applicable to the trend in α values observed here. Creation of partial charges in the transition state will lead to repulsion of the low dielectric hydrocarbon "tail" thus reducing solvent exclusion at the reaction center in the long chain esters. Less charge separation will then be required in the transition state to effect sufficient solvation to stabilize the intermediate—hence the lower value of the α term. The series of α values corresponding to variation of the *p*-group for constant ester alkyl group (Table III (*e*)) is most unexpected. We have assumed, however,

TABLE III

α VALUES FOR BENZENESULPHONIC ESTERS

Ester		α	Δα
(*a*) *p*H series			
Me-*p*H*		0	
			19
Et-*p*H		19	
			23
*n*Pr-*p*H		26	
			21
*n*Bu-*p*H		10	
*n*Pen-*p*H		11	
(*c*) *p*Br series			
Me-*p*Br		7	
			19
Et-*p*Br		26	
			21
*i*Pr-*p*Br		47	
(*e*) Me-*p*X series			
Me-*p*H	1.8†	0	
Me-*p*Br	1.7†	7	
Me-*p*NO_2	4.3†	9	
Me-*p*F	4.3†	13	
Me-*p*Me	6.2†	15	
Me-*p*MeO		20	

Ester	α	Δα
(*b*) Branched chain series		
Me-*p*H	0	
		19
Et-*p*H	19	
		23
*i*Pr-*p*H	42	
		21
*i*Bu-*p*H	63	
*neo*Pen-*p*H	(112)	
(*d*) *p*NO_2 series		
Me-*p*NO_2	9	
		20
Et-*p*NO_2	29	
		21
*i*Pr-*p*NO_2	50	
(*f*) *p*Me series		
Me-*p*Me	15	
		19
Et-*p*Me	34	
		21
*i*Pr-*p*Me	55	

**The nomenclature used in Table III will be clear from the example, Me-pH = methyl benzenesulphonate.*

†*Heat of solution in kcal. of corresponding benzenesulphonic acids in water.*

as a first approximation (see Section 2), that the nature of solvation of the ester molecule at points other than the seat of reaction, the SO_3 group, is relatively the same in both the initial and transition states. This approximation may not be valid when dealing with the effect of *p*-groups since in addition to the intramolecular effect of such groups on the reaction center they may also lead to different solvation at points other than the SO_3 group in the initial and transition states. One interesting comparison which may have significance is that of the α values for these *p*-groups with the heat of solution of the corresponding benzenesulphonic acids (32). This is illustrated in Fig. 5 where it will be noted that both the *p*-F and *p*-Br compounds lie above the line through the other points.

4. *Benzenesulphonic Ester Solvolysis by S_N12 Mechanism*

On the basis of the interpretation of activation energies we have presented, let us consider in greater detail the S_N12 mechanism as it applies to the solvolysis of benzenesulphonic esters. In Fig. 1 we considered the general relationship between S_N12, S_N1, and S_N2 reactions but did not attach significance to the relative heights of the first maxima for each curve. Let us now consider three cases *within* the S_N12 range as depicted in Fig. 6. For example, let these curves

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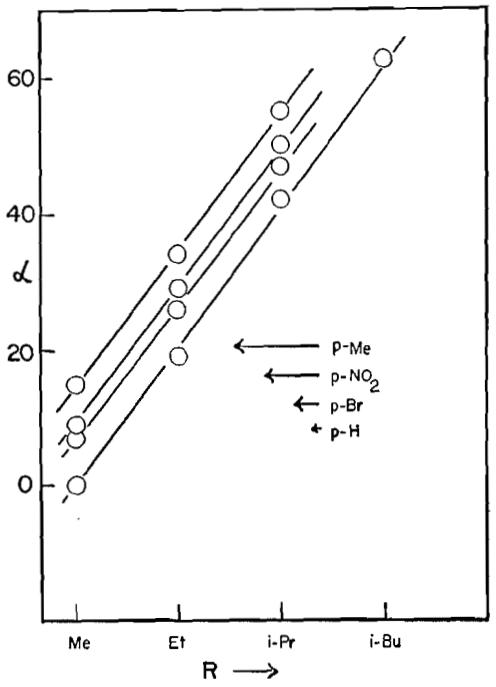

FIG. 3.

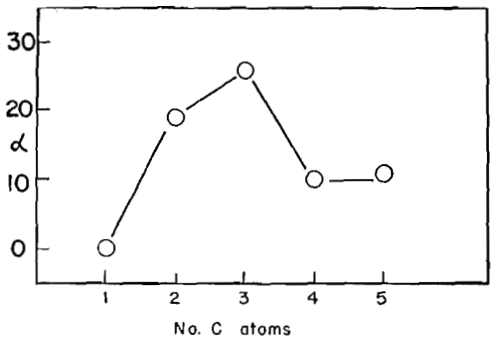

FIG. 4.

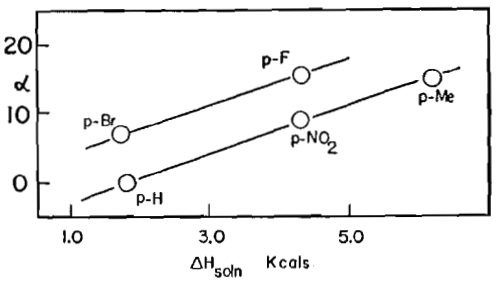

FIG. 5.

represent the relative energy vs. reaction parameter relationship for isopropyl (1), ethyl (2), and methyl (3) benzenesulphonates. In Table IV the observed activation energies and calculated α values are recorded for the hydrolysis of these three esters. Since in the S_N12 mechanism the rate and activation energy are determined in the first transition state the heights of the initial maxima in Fig. 6 are in the order isopropyl > ethyl > methyl benzenesulphonate. The α values indicate greater charge separation for greater activation energy. The greater the charge separation the greater will be the solvation

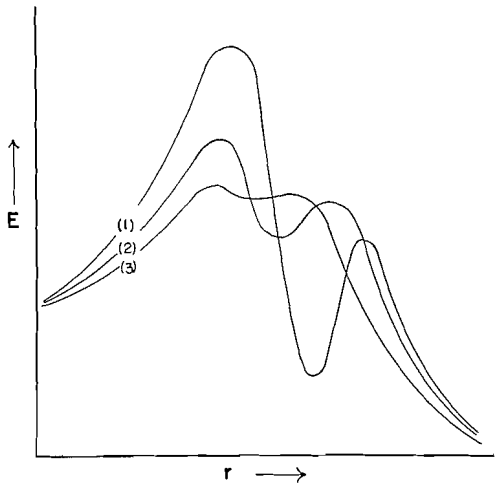

FIG. 6.

TABLE IV

Ester	E_a (cal.)	α
*iso*Pr-*p*H	22,659	42
Et-*p*H	21,040	19
Me-*p*H	20,520	0

stabilization and hence the deeper the intermediate minimum leading in the extreme to the formation of solvation stabilized ions (S_N1). The onset of covalent interaction between solvent molecules and charge separated ester species occurs at an earlier stage along the reaction parameter r as we proceed down the series isopropyl, ethyl, methyl, this covalent interaction requiring higher activation energy as the intermediate becomes less ionic in character. Eventually covalent interaction will enter at such an early stage that an appreciable amount of solvent–solute covalent interaction will take place in the first transition state and the mechanism will become S_N2 in character.

DISCUSSION OF SOLVOLYTIC ACTIVATION ENTROPIES

Discussion of activation entropy must be restricted to a comparison within a series of systems, since in the absence of a knowledge of the collision number we are confined to the use of log PZ as a relative measure of the activation

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entropy (21). We may assume, however, that as log PZ decreases, ΔS becomes a larger negative quantity indicating a greater increase in ordering on moving from initial to transition state.

1. *Series of Varying Ester in Given Solvent*

For the straight chain alkyl group series of esters we find the entropy difference between initial and transition state decreasing as we proceed from methyl to ethyl benzenesulphonate. Table V would indicate that the increased bulk of the ethyl group limits the extent of increase of ordering possible in the transition state despite the increase in attraction offered by the increase in

TABLE V

LOG PZ OF HYDROLYSIS OF BENZENESULPHONIC ESTERS

Ester	log PZ	α
Me-*p*H	10.227	0
Et-*p*H	10.500	19
*n*Pr-*p*H	10.500	26
*n*Bu-*p*H	10.040	10
*n*Pen-*p*H	10.173	11
*iso*Pr-*p*H	13.424	42
*iso*Bu-*p*II	11.483	63

charge separation (α value). The entropy decrease on moving to the transition state will then be less than in the methyl case. Further increase in chain length, viz. to *n*-propyl, sees the onset of chain stiffening. The solvent exclusion effect of the hydrocarbon tail in the transition state is reduced through repulsion of the *n*-propyl chain from the partial charges generated at the reaction center. The increased bulk of the *n*-propyl over ethyl is therefore counterbalanced by chain stiffening and the ΔS (or log PZ) value is approximately equal to that for ethyl; *n*-butyl and *n*-pentyl groups suffer such repulsion from the partial charges that their solvent exclusion effects and hence the ΔS values are comparable with the methyl compound. On considering the branched chain alkyl benzenesulphonic esters we find a very marked reduction in the entropy difference between initial and transition states. By a similar argument to that employed for the straight chain alkyl groups we would conclude that the solvent exclusion effect in the isopropyl case is much increased leading to a marked reduction in increase of ordering in the transition state compared with the initial state again despite the creation of greater partial charges. It is then sterically impossible to accommodate any significantly greater number of molecules in the transition state solvation shell compared with the initial state, leading to a very small entropy change. This does not deny, however, the possibility that the solvation shell molecules are held more rigidly, a phenomenon which, we feel, would be reflected more in the heat capacity change than in the entropy change. As would be expected, the isobutyl case, with branching on the β-carbon atom, shows somewhat less marked solvent exclusion reflected in the greater entropy change compared with isopropyl. It should be noted that generally speaking, the log PZ values follow the same trend as the α values.

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2. *Series of Given Ester in Varying Solvent*

Let us consider the case of solvolysis of methyl *p*-methyl benzenesulphonate in a series of hydroxylic solvents (Table VI).

For a given ester the dipolar initial state will encounter increasing difficulty in ordering progressively larger solvent molecules about it in a solvation shell. As the hydrocarbon residue of the hydroxylic solvent increases in size, therefore, the entropy of the initial state will increase (Fig. 7). A similar condition will obtain in the transition state but the effect of size on degree of ordering will be somewhat reduced owing to the greater attractive force exerted on the solvent molecules by the partial charges created in the transition state. The entropy of the transition state might then be expected to increase less rapidly through the series than in the initial state (Fig. 7). On this picture it is clearly seen that the entropy decrease from initial to transition state increases on moving up the series. This is in agreement with the observed log *PZ* behavior (Table VI).

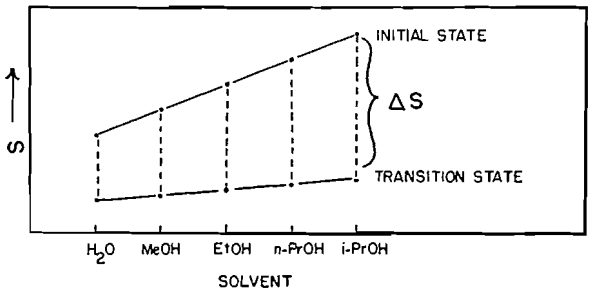

FIG. 7.

TABLE VI

LOG *PZ* OF SOLVOLYSIS OF METHYL *p*-METHYL BENZENESULPHONATE IN VARIOUS SOLVENTS

Solvent	H_2O	MeOH	EtOH	*n*PrOH	*iso*PrOH
log *PZ*	10.369	9.494	8.988	8.863	7.806

CONCLUSIONS

The validity of the interpretation of solvolytic activation energies presented in this paper is based upon the success of the derived semiempirical equation in predicting the observed activation energies. The effect of neglect of temperature dependence of activation energy has been considered and in the finer analysis of the data this may be of some importance. The general success of the equation in relating more than fifty activation energies to measurable parameters of the reaction system cannot, however, be denied. Whether the molecular pictures of the successive states occurring in the reaction mechanism proposed can be justified by direct proof of their existence is questionable at the present time. The fact remains, however, that on the basis of the mechanism proposed, physical significance can be given to the form of the semiempirical equation employed and a factor, α, can be derived, the variation of which, through series of solvolyses, appears to be in keeping with the general picture

presented. Much discussion has been centered around the validity of interpreting activation entropies in the manner here adopted. We would not deny that the definition of the physical significance of a single entropy value is a very complex problem but in discussing the significance of a series of entropy differences we feel we have some justification. If this paper does no more than provoke discussion of the mechanistic points presented it will have served its purpose.

A logical extension of the treatment of activation energy data presented here forms the basis for a further paper on solvolysis in mixtures of water with several alcohols. The success of this extension is even more striking than the present correlation and further serves to assure us that the model we have presented is a good first approximation to the truth. At this stage in the interpretation of the energetics of reaction mechanisms one can hardly expect more.

ACKNOWLEDGMENT

We are indebted to Prof. P. M. Laughton of Carleton College, Ottawa, for much helpful discussion and criticism of this work.

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ORGANIC NITRATES AS SYNTHETIC INTERMEDIATES

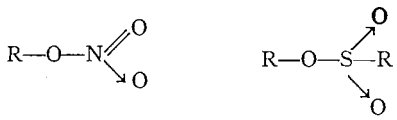
PREPARATIONS OF NITRATES AND SOME REPRESENTATIVE REACTIONS[1]

By F. L. M. Pattison and G. M. Brown[2]

ABSTRACT

It has been shown that the carbon–oxygen bond of nitrate esters is susceptible to cleavage by certain representative nucleophilic reagents, of which sodium iodide, sodium cyanide, and potassium thiocyanate have received particular attention. Allyl, 3-hydroxypropyl, 4-fluorobutyl, hexyl, and benzyl nitrate were examined in order to determine the effect if any of functional groups on the ease and efficiency of cleavage.

Alkyl and aralkyl sulphonates are well known as synthetic intermediates, undergoing most of the replacement and elimination reactions characteristic of the alkyl halides. However, their preparation, while frequently occurring in very high yield, is time consuming, and the products often have very high boiling points, making purification inconvenient. Accordingly, attention was directed to esters of other inorganic oxy-acids; these it was hoped would undergo the same reactions, due to oxygen–alkyl fission. From a superficial consideration of structure, nitrates were selected for study:



The chemistry of nitrate esters has been reviewed recently (3). Several alkylation reactions have been reported: benzyl nitrate has been used successfully in benzylating malonic and acetoacetic esters (15); methyl nitrate has been converted to the corresponding isothiouronium nitrate using thiourea (21); diphenylmethyl nitrate has been converted to N-diphenylmethylacetamide on treatment with acetamide (6); trialkylsulphonium nitrates have been formed from dialkyl sulphides and alkyl nitrates (18); amines have been alkylated using alkyl and aralkyl nitrates (9, 12, 19); and the action of sodium ethoxide on nitrates has produced ethyl ethers (4, 5). The reactions of nitrates have received most attention in the field of carbohydrates, and in at least one instance the nitrate grouping has been replaced by iodide using sodium iodide in acetone (11). No reference has been made to the replacement reactions of the nitrate grouping as a simple alternative to the use of alkyl halides in preparative organic chemistry.

[1]*Manuscript received March 12, 1956.*
Contribution from the Department of Chemistry, University of Western Ontario, London, Ontario. Abstracted from the M.Sc. thesis submitted to the University by G. M. Brown in 1955. Issued as D.R.B. Report No. SW-25.
[2]*Holder of a Scholarship from the Research Council of Ontario, 1954–1955. Present address: Department of Chemistry, Laval University, Quebec, Que.*

Nitrates may be prepared by direct esterification of alcohols with nitric acid, or by reaction of a suitable alkyl halide with silver nitrate. However, only the first of these is of practical importance in this work, since the halides required for the second method could themselves be used directly in the replacement reactions. The direct esterification method has been reported to be very simple and to give high yields, but the conditions are sometimes critical; the halide method gives consistently good results. For convenience, both methods were employed to obtain the nitrate esters used in this work. Results are shown in Table I.

TABLE I

NITRATES: PREPARATION, PHYSICAL CONSTANTS, AND ANALYTICAL RESULTS

R in $RONO_2$	Method of preparation[a]	Yield, %	Boiling point °C.	Boiling point mm.	n_D^{25}	C, % Calc.	C, % Found	H, % Calc.	H, % Found
CH_2:$CHCH_2$–[b]	I	33	102–105		1.4112				
	II	49	104–106		1.4120				
$HO(CH_2)_3$–	I	49	103–104	16	1.4378	29.75	29.83	5.84	5.90
	III	76	123–125	42	1.4372				
$CH_3(CH_2)_3$–[c]	II	54	130–131		1.4031				
	III	61	130–133		1.4030				
	IV	74	130–132		1.4036				
$F(CH_2)_4$–	II	68	74–77	19	1.4060	35.03	34.82	5.89	5.88
	III	75	65	12	1.4070				
$Cl(CH_2)_4$–	III	64	92–93	11	1.4541	31.28	30.93	5.26	4.92
$CH_3(CH_2)_5$–[d]	II	83	66–70	12	1.4174				
	III	77	66	11	1.4180				
	IV	73	67–69	12	1.4182				
$F(CH_2)_6$–	II	28[h]	112	28	1.4179	43.62	43.82	7.34	7.35
$C_6H_5CH_2$–[e]	I	70	101–104	12	1.5179				
$CH_3(CH_2)_9$–[f]	IV	59	127–128	12	1.4328				
$CH_3(CH_2)_{11}$–[g]	IV	67	143–144	5	1.4380				

[a] *Methods of preparation—I: chloride+silver nitrate; II: bromide+silver nitrate; III: iodide +silver nitrate; IV: alcohol+HNO_3 and H_2SO_4.*

[b] *Henry (10) reports b.p. 106°.*

[c] *Cowley and Partington (7) report b.p. 135.7° at 770 mm. and n_D^{20} 1.4063.*

[d] *Soffer, Parrotta, and Di Domenico (20) report b.p. 46° at 1 mm. and $n_D^{24.5}$ 1.4180.*

[e] *Lucas and Hammett (13) report b.p. 72.5–73.5° at 4–5 mm. and n_D^{25} 1.5180.*

[f] *Medard and Alquier (14) report b.p. 88–89° at 1–2 mm.*

[g] *Medard and Alquier (14) report b.p. 99–100° at 1–1.5 mm.*

[h] *Low yield due to accidental loss.*

The cleavage of nitrates is significant in the main as a method of replacing –OH by different functional groups, that is, as an alternative to the use of halides or sulphonates. Some representative cleavages are shown in Table II. In addition to those listed, benzyl nitrate was treated (*a*) with sodium bromide

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to form benzyl bromide in 64% yield, and (*b*) with thiourea followed by hydrolysis to form benzyl mercaptan in 32% yield. Analytical results and physical constants of new compounds are listed in Table III. The boiling points of some of the products were very similar to those of the parent nitrates, making purification difficult.

TABLE II

CLEAVAGE OF NITRATES: YIELDS (%)

Reaction	R = CH_2:$CHCH_2$–	HO$(CH_2)_3$–	F$(CH_2)_4$–	$CH_3(CH_2)_5$–	$C_6H_5CH_2$–
$RONO_2 + NaI \rightarrow RI + NaNO_3$	62	60	63	84	76
$RONO_2 + NaCN \rightarrow RCN + NaNO_3$	31[a]	—	45[a]	77[b]	68[a]; 66[b]
$RONO_2 + KSCN \rightarrow RSCN + KNO_3$	33[c]	35	57	86	86

[a]*80% Ethanol as solvent.*
[b]*Ethylene glycol as solvent.*
[c]*Allyl isothiocyanate.*

TABLE III

PRODUCTS OF CLEAVAGE: PHYSICAL CONSTANTS AND ANALYTICAL RESULTS OF NEW COMPOUNDS

	Boiling point		n_D^{25}	C, %		H, %		Other, %	
	°C.	mm.		Calc.	Found	Calc.	Found	Calc.	Found
HO$(CH_2)_3$I	99–100	20	1.5480	19.37	19.65	3.80	3.81	I, 68.23	I, 68.10
HO$(CH_2)_3$SCN	143–144	14	1.4688	41.00	40.97	6.03	6.10	N, 11.96	N, 11.66
F$(CH_2)_4$I	53–54	13	1.4940					I, 63.78	I, 64.08
F$(CH_2)_4$CN	72	10	1.3963					F, 18.81	F, 18.6
F$(CH_2)_4$SCN	100–101	13	1.4611	45.11	44.96	6.01	5.90	N, 10.52	N, 10.35

In view of the ready conversion of halides and sulphonates to fluorides by potassium fluoride (16, 17), a representative nitrate was examined under conditions similar to those reported. On heating hexyl nitrate at 110° for eight hours with potassium fluoride in diethylene glycol, low yields (10–15%) of hexyl fluoride were obtained. From this preliminary observation, it seems unlikely that nitrates will be used extensively in the preparation of aliphatic fluorides.

In compounds containing both sulphonate and halogen groups, the former have been shown to be preferentially replaced relative to the latter (17), as for example in the conversion of 4-chlorobutyl methanesulphonate by potassium thiocyanate to 4-chlorobutyl thiocyanate in 67% yield. This was not possible with ω-haloalkyl nitrates; under the conditions necessary to replace the nitrate grouping, the halogen was also replaced.

From limited observations, alkyl nitrites proved to be useless as alternatives to nitrates in the replacement reactions described above. Under conditions similar to those used for converting hexyl nitrate to hexyl iodide, hexyl nitrite formed *n*-hexanol.

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The preliminary results presented in this paper indicate that alkyl nitrates are of potential value as synthetic intermediates, while not offering any particular advantages over the well-known alkyl halides and sulphonates. It is hoped to examine the cleavage of nitrates in more complex molecules in order to assess the versatility and scope of the reaction.

EXPERIMENTAL[3]

(*a*) *Preparation of Intermediates*

Trimethylene iodohydrin.—Trimethylene chlorohydrin (20 gm., 0.21 mole), sodium iodide (63 gm., 0.42 mole), and anhydrous acetone (200 ml.) were heated under reflux for 13 hr. Most of the acetone was removed by distillation. After the mixture had been cooled and diluted with water, the product was extracted with ether. The extract was dried over anhydrous sodium sulphate. The ether was removed, and the residue on fractional distillation from freshly prepared silver crystals yielded trimethylene iodohydrin (19.7 gm., 50%) of b.p. 105° at 25 mm. and n_D^{25} 1.5480.

4-Fluorobutyl bromide, 4-fluorobutyl iodide, and 6-fluorohexyl bromide have been described elsewhere (16).

4-Chlorobutyl iodide was prepared from 1,4-dichlorobutane using sodium iodide in acetone (1).

(*b*) *Preparation of Nitrates*

The four methods summarized in Table I are represented by the following examples.

Method I: Benzyl nitrate.—Benzyl chloride (80 gm., 0.63 mole) was added over a period of 10 min. to silver nitrate (130 gm., 0.76 mole) in anhydrous acetonitrile (150 ml.). The mixture was then heated under reflux for 50 min. The silver chloride was removed by filtration and washed with a small quantity of acetonitrile. After removal of the acetonitrile at a temperature of less than 90°, the residue on distillation yielded benzyl nitrate (68.4 gm., 70%).

Method II: n-Hexyl nitrate.—*n*-Hexyl bromide (84.5 gm., 0.51 mole) was slowly added to a solution of silver nitrate (116 gm., 0.68 mole) in anhydrous acetonitrile (110 ml.) and the resultant mixture was allowed to stand at room temperature for 15 hr. After removal of the silver bromide by filtration, the mixture was heated under reflux for one hour. The solution was cooled and filtered, and then diluted with water (250 ml.). The crude nitrate was extracted with ether and the extract dried over anhydrous sodium sulphate. After removal of the ether, *n*-hexyl nitrate (62.5 gm., 83%) was obtained as a colorless liquid.

Method III: 4-Fluorobutyl nitrate.—4-Fluorobutyl iodide (47.0 gm., 0.23 mole) was slowly added to silver nitrate (42.5 gm., 0.25 mole) in anhydrous acetonitrile (60 ml.) with external cooling provided by an ice bath. The mixture was allowed to stand at room temperature for 19 hr., was filtered, and then the solvent removed. The residue on distillation yielded 4-fluorobutyl nitrate (23.8 gm., 75%).

[3]*Physical constants and analytical data are listed in Tables I and III.*

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Method IV: n-Butyl nitrate.—Concentrated sulphuric acid (76.8 ml., specific gravity 1.84, 95% by weight) was slowly added at a temperature of less than 10° to a mixture of urea (2.5 gm.) and concentrated nitric acid (76.8 ml., 1.2 moles, specific gravity 1.42, 70% by weight). The resultant solution was cooled to 0° in an ice–HCl bath, and *n*-butyl alcohol (44.4 gm., 0.60 mole) was added with vigorous stirring at the rate of about 1 ml. per min. When the addition was complete, the mixture was stirred for a further 15 min. and then diluted with water. The nitrate layer was washed three times with 10% aqueous potassium carbonate and then with water. After it was dried over anhydrous sodium sulphate, distillation yielded *n*-butyl nitrate (52.8 gm., 74%) as a colorless, pleasant-smelling liquid.

(*c*) *Cleavages of Nitrates*

The following examples are representative of the cleavages of nitrates.

n-Hexyl iodide.—*n*-Hexyl nitrate (8.0 gm., 0.054 mole), sodium iodide (16.2 gm., 0.108 mole), and anhydrous acetone (40 ml.) were heated under reflux for 27 hr. The solvent was removed by distillation below 58°, and the residue was diluted with water (100 ml.) and extracted with ether. The extracts were washed successively with water, aqueous sodium thiosulphate, and water. They were then dried over anhydrous sodium sulphate and the ether was removed; the residue on distillation yielded *n*-hexyl iodide (9.7 gm., 84%), b.p. 60–63° at 12 mm., n_D^{25} 1.4894.

n-Heptanonitrile.—*n*-Hexyl nitrate (10.0 gm., 0.068 mole), sodium cyanide (3.4 gm., 0.070 mole), and ethylene glycol (20 ml.) were stirred at reflux temperature for two hours. The reddish-brown reaction mixture was diluted with water (200 ml.) and extracted with ether. The extracts were washed successively with 4 *N* hydrochloric acid (to remove traces of the isonitrile), aqueous sodium bicarbonate, and water, and dried over anhydrous magnesium sulphate. The ether was removed, and the residue on distillation yielded *n*-heptanonitrile (5.8 gm., 77%), b.p. 98° at 39 mm., n_D^{25} 1.4135.

4-Fluorobutyl thiocyanate.—4-Fluorobutyl nitrate (6.0 gm., 0.044 mole), potassium thiocyanate (12.8 gm., 0.132 mole), and 95% ethanol (50 ml.) were heated under reflux for 12 hr. The mixture was cooled, diluted with water (200 ml.), and extracted with ether. The extracts were washed with saturated calcium chloride and with water, and then dried over anhydrous sodium sulphate. After removal of the ether, the residue on distillation yielded 4-fluorobutyl thiocyanate (3.3 gm., 57%), a colorless, vile-smelling liquid.

Benzyl bromide.—A mixture of benzyl nitrate (6.0 gm., 0.039 mole), sodium bromide (12.1 gm., 0.117 mole), and anhydrous acetone (125 ml.) was heated under reflux with stirring for 26 hr. After the usual isolation procedure (removal of acetone, dilution with water, ether extraction, and drying), benzyl bromide (4.3 gm., 64%) was obtained as a colorless, lachrymatory liquid of b.p. 81–83° at 14 mm. and n_D^{25} 1.5690; Baker (2) reports b.p. 85° at 13 mm.

Benzyl mercaptan.—Benzyl nitrate (15.3 gm., 0.10 mole), thiourea (7.2 gm., 0.095 mole), and 95% ethanol (20 ml.) were heated under reflux for 4.5 hr. The cooled mixture was diluted with water (75 ml.) and the crude benzyl isothiouronium nitrate was collected by filtration. A small sample, recrystallized

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from water, had m.p. 120–120.5°; Taylor (21) reports m.p. 118–119°. To the crude solid was added a solution of sodium hydroxide (8.0 gm., 0.20 mole) in water (80 ml.), and the mixture was heated under reflux for four hours. After it had been cooled and acidified with 3 *N* hydrochloric acid (75 ml.), the solution was extracted with ether. The extract was washed with aqueous sodium bicarbonate and with water, and dried over anhydrous sodium sulphate. After removal of the ether, the residue on distillation yielded benzyl mercaptan (3.8 gm., 32%) of b.p. 88–89° at 18 mm. and n_D^{25} 1.5723; Farlow and Signaigo (8) report b.p. 99° at 32 mm. and n_D^{25} 1.5729.

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THE REACTION OF ACTIVE NITROGEN WITH MERCURY DIETHYL[1]

By D. A. Armstrong[2] and C. A. Winkler

ABSTRACT

The main organic product of the reaction was hydrogen cyanide, the maximum yield of which was practically independent of temperature in the range 130° to 330°C., and appeared to correspond to about one-half the active nitrogen concentration present. Presumably the reactant or products, or both, caused deactivation of about one-half the active nitrogen. Small amounts of butane, propane, ethane, methane, propylene, ethylene, acetylene, and cyanogen were also found in the products.

INTRODUCTION

The results of a previous study with azomethane (1) indicated that the methyl radical – active nitrogen reaction is very fast and characterized by a low activation energy. The present investigation was made to determine whether the reactions of active nitrogen with metal alkyls might give useful information about active nitrogen – free radical reactions.

EXPERIMENTAL

The apparatus and analytical procedures were similar to those outlined in the earlier paper. The molecular nitrogen flow rate was 9.75×10^{-5} mole/sec. throughout, while the mercury diethyl flow was varied between 0.5×10^{-6} and 10^{-5} mole/sec. Pressures in the reaction vessel were 0.90 to 0.95 mm.

RESULTS AND DISCUSSION

The reaction gave a lilac-colored flame at all flow rates and temperatures, and caused the temperature to increase in the uncovered reaction vessel from 53°C. (active nitrogen alone) to about 130°C.

Hydrogen cyanide was the main organic product of the reaction. Mass spectrometric analysis of the fraction taken from a LeRoy still (2) at −155°C. showed the presence of small quantities of propane, ethane, ethylene, propylene, and acetylene. Similar analysis of two samples of non-condensable gas from the reaction at 350°C. indicated methane to the extent of about 5% of the HCN, and hydrogen roughly equivalent to the HCN. Small quantities of cyanogen and butane were also detected in the reaction products but were not estimated quantitatively. Polymer formation in the reaction vessel was negligible at all temperatures.

The relations between the product yields and mercury diethyl flow rate are shown in Fig. 1. The carbon balances were generally poor; they fell as low as

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[2]*Holder of National Research Council Studentship, 1953–54, and Cominco Fellowship, 1954–55.*

73% and rarely exceeded 90%. The difficulty appeared to be in obtaining satisfactory recovery of the unreacted mercury diethyl.

As in previous papers, the results may be discussed on the basis that atomic nitrogen is the main reactive species in active nitrogen.

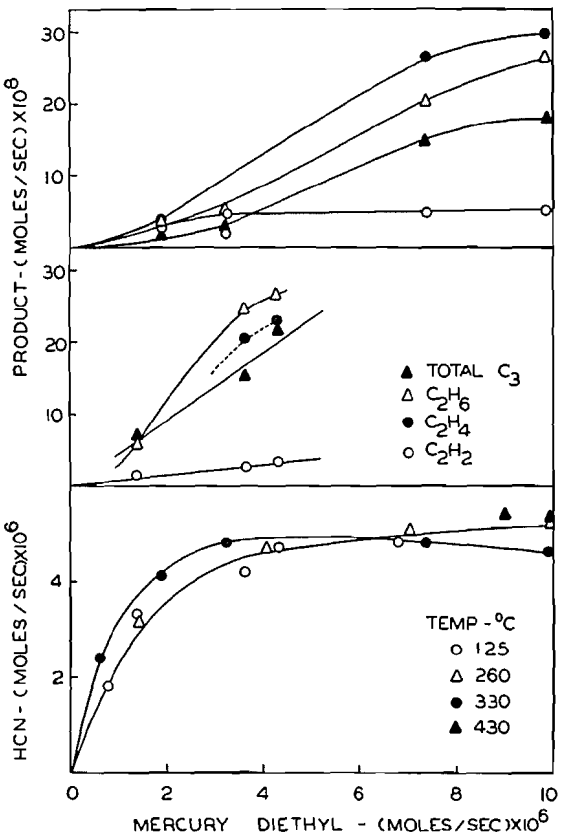

FIG. 1. Relation of product yields to mercury diethyl flow rate. Top curves at 330°C. Middle curves at 125°C.

The maximum production of hydrogen cyanide from mercury diethyl was roughly one-half the maximum amount obtained from ethylene in the same apparatus under comparable conditions. It would seem, therefore, that extensive recombination of nitrogen atoms was promoted in the mercury diethyl reaction. Moreover, the relative temperature independence of the maximum hydrogen cyanide yield indicates that the activation energies for the reactions leading to hydrogen cyanide production and to recombination were approximately the same, and probably quite low.

Recombination of nitrogen atoms was probably catalyzed to some extent by mercury atoms, since traces of mercury nitride were indicated by formation

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of titratable base when water was added to the small amounts of residue that remained in the trap after distillation. Recombination could also result from the probable primary reaction

$$N + Hg(C_2H_5)_2 \rightarrow C_2H_5 + N.Hg.C_2H_5,$$

followed by

$$N + N.HgC_2H_5 \rightarrow N_2 + Hg + C_2H_5,$$

and possibly, to some extent, by

$$\begin{aligned} N + N.HgC_2H_5 &\rightarrow N_2 + Hg + C_2H_4 + H \\ &\rightarrow N_2 + Hg + C_2H_2 + H_2 + H \end{aligned}$$

since ethylene and acetylene were found in the products.

The presence of only small quantities of butane in the products indicates that ethyl radicals, like methyl radicals, (1), react rapidly with nitrogen atoms, probably by one or more of the following reactions:

$$\begin{aligned} N + C_2H_5 &\rightarrow HCN + CH_3 + H \\ &\rightarrow HCN + CH_2 + H_2 \\ &\rightarrow \ CN + CH_3 + H_2. \end{aligned}$$

Free radical and hydrogen atom reactions would lead to the small amounts of various secondary products obtained.

Owing to the marked deactivation of active nitrogen observed in the present study, it would seem that metal alkyls are not a particularly satisfactory source of radicals for study of active nitrogen – free radical reactions.

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THE ULTRAVIOLET ABSORPTION SPECTRA OF METHYL-1,2-BENZANTHRACENES[1]

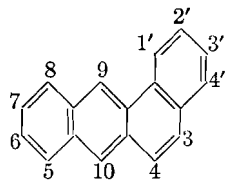
By C. Sandorfy[2] and R. Norman Jones

ABSTRACT

The ultraviolet absorption spectra of 1,2-benzanthracene, all twelve monomethyl derivatives, and six dimethyl derivatives have been measured (*a*) at room temperature in *n*-heptane solution, (*b*) at −100°C. in *n*-pentane solution. An analysis of the band envelopes indicates that most of the absorption between 33,000 and 25,000 cm.$^{-1}$ arises from two series of overlapping bands. The members of each series are spaced at intervals of approximately 1400 cm.$^{-1}$. The spacing between the two band series and their relative intensities are dependent on the nature and position of the alkyl substituents. Absorption between 40,000 and 33,000 cm.$^{-1}$ can be treated in a similar manner. Other fine structure is also observed. It is considered most probable that each of the overlapping series of bands is associated with a separate electronic excitation. The significance of these observations is considered in relation to the theoretical treatments of the energy levels of 1,2-benzanthracene as developed by Klevens and Platt and by Moffitt.

INTRODUCTION

The ultraviolet absorption spectra of 1,2-benzanthracene (I) and of a number of its alkyl derivatives were measured several years ago by Mayneord and



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Roe (23) and by Jones (11), using photographic recording techniques with Hilger Spekker photometers. Similar studies have since been carried out by Badger, Pearce, and Pettit (1) and by Friedel and Orchin (8) using photoelectric spectrophotometers. These investigations were made in ethanol solution at room temperature. The later work revealed little additional structure in the absorption bands, and it is evident that instrumental insufficiencies were not a serious factor in limiting the resolution of the vibrational fine structure.

In the present investigation, the spectra of 1,2-benzanthracene, all twelve monomethyl derivatives, and six dimethyl derivatives have been studied both at room temperature in *n*-heptane solution, and at −100°C. in *n*-pentane solution. Considerably more structure is revealed in the low temperature spectra, and an analysis of the bands has provided additional information about the energy levels of the 1,2-benzanthracene ring system.

[1]*Manuscript received March 7, 1956.*
Contribution from the Division of Pure Chemistry, National Research Council, Ottawa, Canada. Presented in part at a Symposium on Molecular Structure and Spectroscopy, The Ohio State University, June 1952, and at a meeting of The Photoelectric Spectrometry Group, Imperial College, London, England, June 1954. Issued as N.R.C. No. 3968.
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EXPERIMENTAL

The measurements in *n*-heptane were carried out with a Cary spectrophotometer (Model 11 M) operated in the conventional manner. Quartz cells of 1 cm. path length were used, and the cell lengths were calibrated with potassium chromate solution (9). The hydrocarbon (2–3 mgm.) was weighed on a microbalance, dissolved in approximately 10 ml. of *n*-heptane, and the solution weighed to 0.1 mgm. From this primary solution, secondary and tertiary solutions of 1/10 and 1/100 of the initial concentration were prepared gravimetrically. These manipulations were carried out in a constant temperature room at 22°C. and the molarities computed on the basis of a density of 0.684 for all solutions. The *n*-heptane was purified by chromatographic adsorption on silica gel. The maximal extinction coefficients were checked by measurements on duplicate solutions. A mean variation of $\pm 1\%$ was observed in separate determinations. The spectrometer wavelength scale was calibrated against a mercury arc spectrum and neon and argon emission spectra. To facilitate the band analysis, the spectra were subsequently replotted on a linear scale of wave number.

The spectra in *n*-pentane solution were measured on the Cary spectrophotometer using the low temperature cell described by Jones and Keir (13). In these measurements intensities are less accurate because of the errors in the reproducibility of the solvent correction curve and the correction factor for change of the specific gravity of the solution with temperature. These errors

TABLE I

SOURCE AND MELTING POINT CHARACTERIZATION OF 1,2-BENZANTHRACENE AND DERIVATIVES

Compound	M.P.	Source*
1,2-Benzanthracene	158.5–160.5	1
1′-Methyl-1,2-benzanthracene	137.6–138.5	3
2′-Methyl-1,2-benzanthracene	150.6–151.4	3
3′-Methyl-1,2-benzanthracene	163.3–164.0	3
4′-Methyl-1,2-benzanthracene	196.0–197.0	3
3-Methyl-1,2-benzanthracene	155.8–156.4	3
4-Methyl-1,2-benzanthracene	126.9–127.4	3
5-Methyl-1,2-benzanthracene	159.4–159.6	3
6-Methyl-1,2-benzanthracene	152.3–152.8	3
7-Methyl-1,2-benzanthracene	185.1–185.4	3
8-Methyl-1,2-benzanthracene	118.0–118.4	3
9-Methyl-1,2-benzanthracene	139.0–139.4	3
10-Methyl-1,2-benzanthracene	140.0–140.5	3
1′,10-Dimethyl-1,2-benzanthracene	124 –125	1[a]
2′,6-Dimethyl-1,2-benzanthracene	163 –164	2[b]
2′,7-Dimethyl-1,2-benzanthracene	240.2–240.5	2[b]
3′,6-Dimethyl-1,2-benzanthracene	186.0–186.5	2[b]
3′,7-Dimethyl-1,2-benzanthracene	189 –190	2[b]
9,10-Dimethyl-1,2-benzanthracene	122.7–123.4	1
1′,9-Methylene-1,2-benzanthracene	121.5–122.0	1[c]

*1. *L. F. Fieser, Harvard University.*
*2. *J. W. Cook, Chester Beatty Research Inst., London, England.*
*3. *M. S. Newman, The Ohio State University.*
[a]*See Reference 7.*
[b]*See Reference 4.*
[c]*See Reference 6.*

cannot be evaluated precisely but are probably of the order of $\pm 5\%$ at the absorption maxima. The melting points and sources of the compounds are listed in Table I. The values reported for the positions of the absorption maxima are accurate to ± 20 cm.$^{-1}$ on sharp bands, but the uncertainty increases as the bands become more diffuse.

RESULTS

The curves reproduced in this paper have been selected to illustrate points which arise in the discussion. A separate bulletin (14) will be published which will contain the complete collection of curves, together with tables of the positions of the absorption maxima for the *n*-pentane solutions at $-100°$, and tables of the intensities and positions of the maxima for the *n*-heptane solutions at room temperature.

In ethanol solution at room temperature, 1,2-benzanthracene exhibited 12 absorption maxima between 43,000 and 25,000 cm.$^{-1}$. In an earlier publication (11) we labelled these bands *A–I*, *I'*, *J*, *K* as shown in Fig. 1. Intensity con-

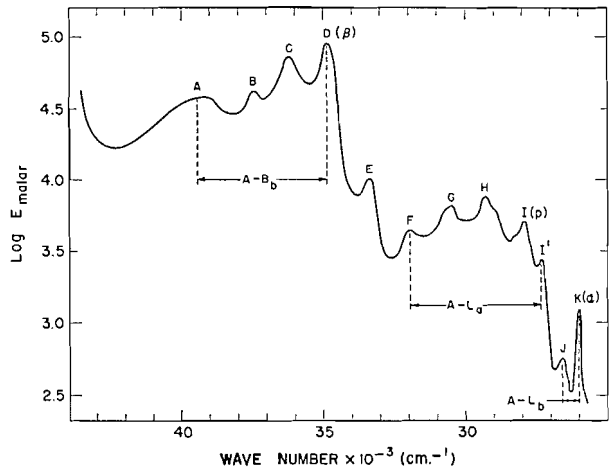

FIG. 1. Ultraviolet absorption spectrum of 1,2-benzanthracene in ethanol solution at room temperature. The nomenclature systems used by Clar (3), Jones (11), and Klevens and Platt (18) are indicated.

siderations suggested that the *A–D*, *F–I'*, and *J–K* bands probably constituted three separate groups. Klevens and Platt (18) have assigned these groups of bands to transitions from the ground state to three different electronic energy levels. These they designate B_b, L_a, and L_b in their system of nomenclature, which is based on a molecular orbital treatment of a free electron moving around the perimeter of the molecule. Clar (3) has identified our bands *D*, *I*, and *K* with β, *p*, and α in his nomenclature system, which is based on an empirical treatment of the band shifts with changes in "Anellierung". Other systems of nomenclature are used by Coulson (5) and by Moffitt (24).

Room Temperature Spectra in n-Heptane

The spectrum of 1,2-benzanthracene in *n*-heptane at room temperature is shown in Fig. 2. On the introduction of methyl substituents changes occur in

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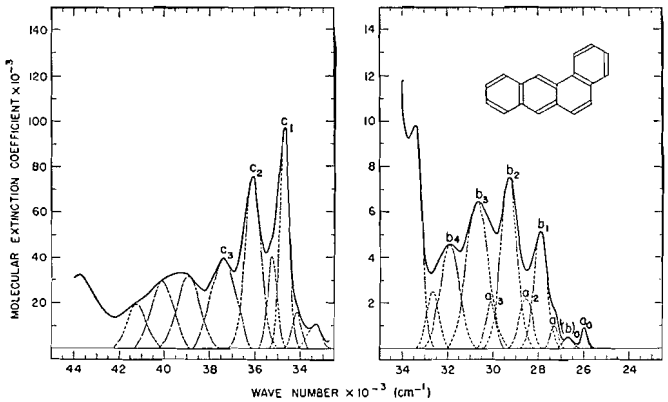

FIG. 2. Ultraviolet absorption spectrum of 1,2-benzanthracene in *n*-heptane solution at room temperature.

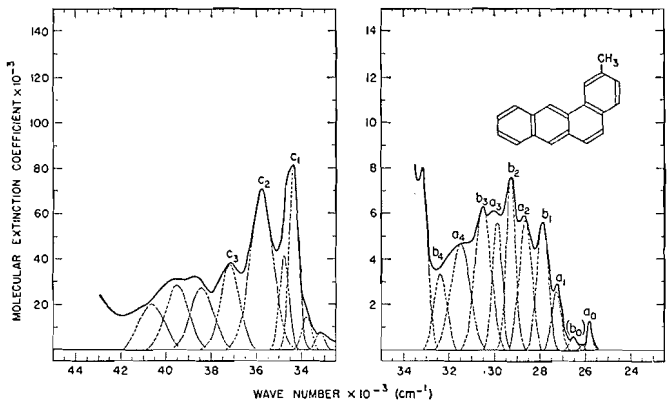

FIG. 3. Ultraviolet absorption spectrum of 2′-methyl-1,2-benzanthracene in *n*-heptane solution at room temperature.

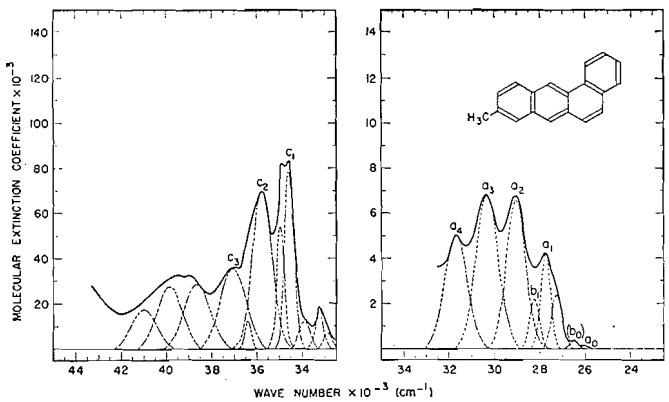

FIG. 4. Ultraviolet absorption spectrum of 6-methyl-1,2-benzanthracene in *n*-heptane solution at room temperature.

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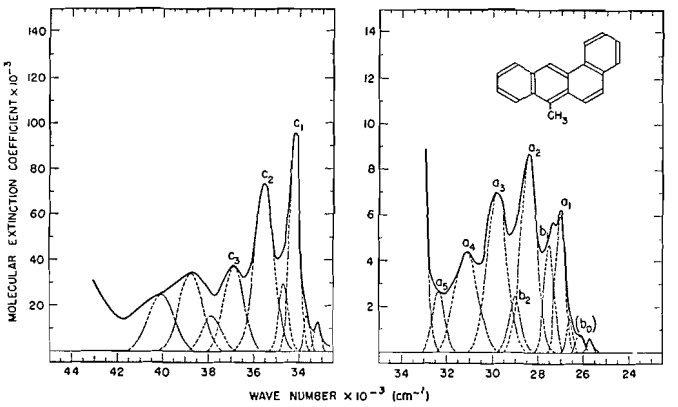

FIG. 5. Ultraviolet absorption spectrum of 10-methyl-1,2-benzanthracene in *n*-heptane solution at room temperature.

the band contours. The curves for the 2′-methyl, 6-methyl, and 10-methyl derivatives, shown in Figs. 3–5, are typical examples. The 2′-methyl and 10-methyl spectra have been chosen to illustrate the more highly and less highly inflected types of band envelope in the 33,000–25,000 cm.$^{-1}$ region. Neither of these two is highly inflected at higher frequencies, but additional structure is exhibited near 35,000 cm.$^{-1}$ in the spectrum of the 6-methyl compound shown in Fig. 5.

In a first attempt to investigate this structure systematically, the band envelopes were analyzed in terms of a series of Gauss curves.

This method of curve analysis has been employed by earlier investigators (2, 19, 16, 17). It is assumed that the envelope can be represented by a series of functions of the form

$$[1] \qquad \epsilon = \epsilon_{max} \exp[-\{(\nu-\nu_0)/h\}^2]$$

where the constants h, ϵ_{max}, and ν_0, indicated in Fig. 6, can be chosen to conform with a selected band.

In applying the method, the absorption peaks of most symmetrical appearance are first fitted by appropriate Gauss curves. The difference between these Gauss curves and the observed band envelope is next plotted and a second series of Gauss curves constructed to fit the most symmetrical peaks of the difference curve. These are in turn subtracted out and the process repeated as often as necessary. In selecting the most suitable Gauss functions, qualitative consideration is given to the displacement effects of overlap on the positions of the band maxima. These were established from analytical studies similar to those made by Vandenbelt and Henrich (29).

Examples of such curve analyses are shown in Figs. 2–5. The complete series of curves for the monomethyl-1,2-benzanthracenes were analyzed in this fashion and in spite of the differences in the complexity of the band contours, it was observed that in the majority of cases approximately the same number of Gauss curves were required, namely 10 or 11 for the 33,000–25,000

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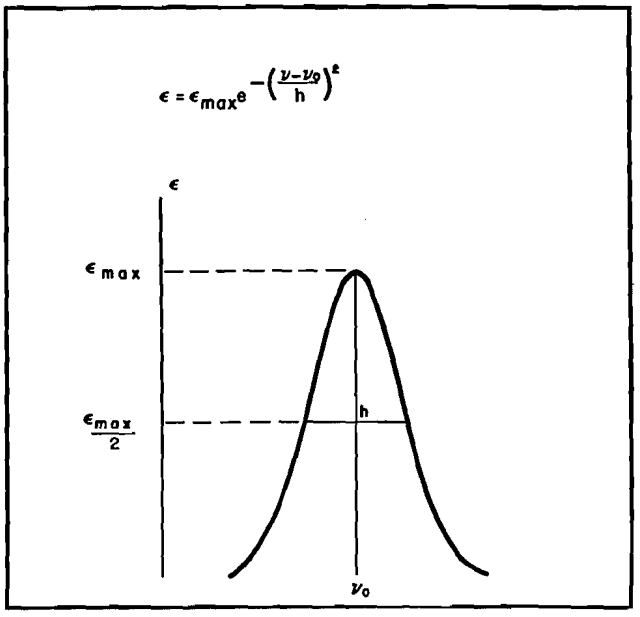

FIG. 6. The Gauss function.

cm.$^{-1}$ region and about eight for the 40,000–33,000 cm.$^{-1}$ region. Since there are arbitrary elements in the selection of the parameters, these do not represent unique analyses of the band envelopes. Nevertheless a comparison of the spacing and intensity of the Gauss curves indicates that between 33,000 and 25,000 cm.$^{-1}$ the spectra consist essentially of two overlapping systems of bands; these we have designated the *a* and *b* band series. The members of each series are spaced at intervals of approximately 1400 cm.$^{-1}$. In the individual compounds these overlapping series differ in their relative intensity and phase relationship. When both are of comparable intensity and the phase separation is great the band envelope appears complex (Fig. 3) but if one series is of predominating intensity or the phase difference is small the contour is simpler (Fig. 5). Between 38,000 and 33,000 cm.$^{-1}$ there is one well-defined set of bands, the *c* series, also with approximately 1400 cm.$^{-1}$ spacing, and possibly also a second one.

Low Temperature Spectra in n-Pentane

In the low temperature spectra these band series can usually be recognized on inspection. The low temperature spectra of 1,2-benzanthracene and of the 2′-methyl, 6-methyl, and 10-methyl derivatives are shown in Figs. 7–10, together with diagrams of the proposed schematic breakdown into band series. Similar diagrams for all the compounds are included in Reference 14 together with tables of the frequencies of the individual spacings in the band series.

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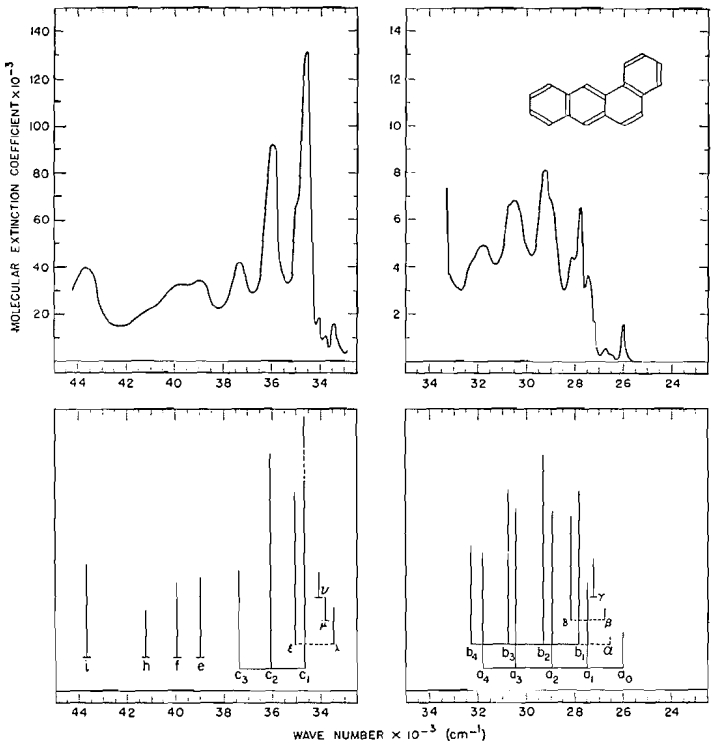

FIG. 7. Ultraviolet absorption spectrum of 1,2-benzanthracene in *n*-pentane solution at −100°C.

In addition to these three main series of bands, several other bands are observed in most of the spectra. These can be considered in three groups: (i) seven bands (α–η) overlapping the *a* and *b* series; (ii) nine bands (λ–τ) overlapping the *c* series; (iii) five bands (*e*–*i*) between 44,000 and 38,000 cm.$^{-1}$. Although this complete set of 21 bands is not observed in the spectrum of any single compound, collectively it accounts for the observed maxima and significant inflections in all the compounds and on this basis the generalized schematic diagram shown in Fig. 11 is proposed.

Comparison of the spacings between the "Greek letter" bands suggests that they probably include at least one additional series in the 38,000–33,000 cm.$^{-1}$ region. This is composed of bands λ, ξ, and ρ, and will be treated as a tentative *d* series in the discussion which follows. In many of the compounds spacings in the range between 1200 and 1500 cm.$^{-1}$ are commonly observed between certain of the Greek letter bands as indicated by the dotted lines in Fig. 11. This figure has been constructed in a manner to emphasize these relationships, but these bands are often diffuse and the similarity of the spacings may be in part fortuitous. For detailed numerical analyses see Table I of Reference 14.

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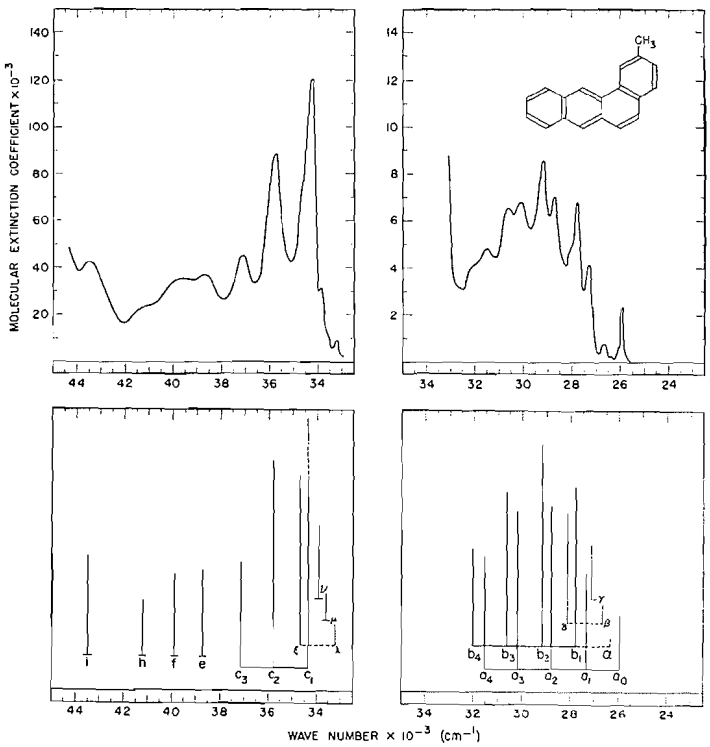

FIG. 8. Ultraviolet absorption spectrum of 2′-methyl-1,2-benzanthracene in *n*-pentane solution at −100°C.

In the schematic diagrams, the height of the line corresponds to the total intensity of the band envelope, and does not make allowance for contributions from overlap with neighboring bands. From this point of view the Gauss curves provide a truer picture of the intensity relationships between the band series, and the best analysis of the spectra would result from Gauss analysis of the low temperature curves. The process is tedious, however, and has not yet been carried out. In some cases it has been observed that the Gauss analysis successfully predicts bands that are not apparent on visual observation of the room temperature spectra. Thus the bands near 34,600, 32,700, 29,000, and 26,500 cm.$^{-1}$ in the Gauss analysis of the spectrum of 10-methyl-1,2-benzanthracene shown in Fig. 5 are resolved as bands o, a_5, b_2, and γ in the low temperature spectrum (Fig. 10).

The a and b Series

In most of the spectra, the middle members of these series show the highest intensities. The two series are most sharply differentiated in the spectra of the 2′-methyl, 3-methyl, 4-methyl, 7-methyl, 2′,7-dimethyl, and 3′,7-dimethyl compounds. The separation tends to become less clear at the higher frequencies where the *b* band may be reduced to an inflection on the side of the *a* band, as

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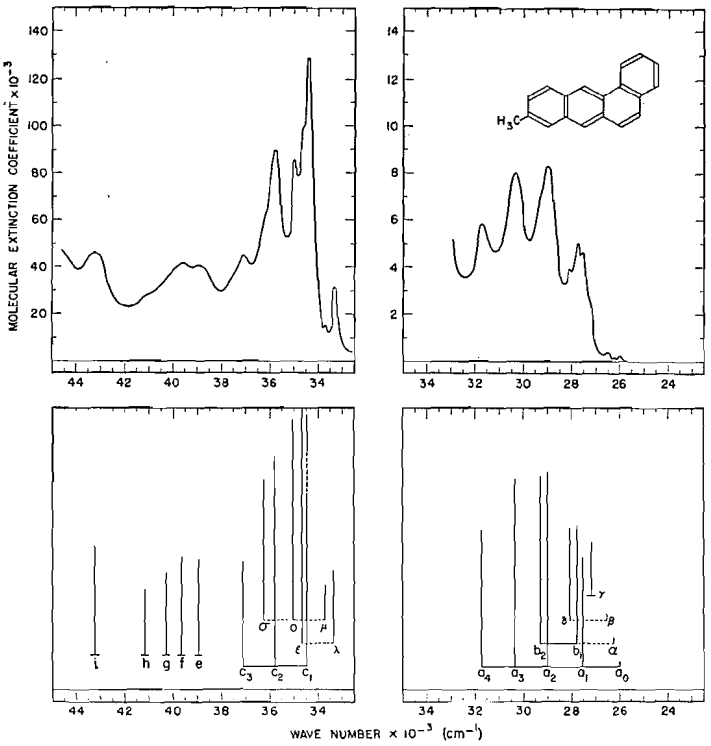

FIG. 9. Ultraviolet absorption spectrum of 6-methyl-1,2-benzanthracene in *n*-pentane solution at −100°C.

is the case for the 5-methyl, 8-methyl, 10-methyl, and 2′,6-dimethyl spectra. The *a* band series can usually be followed out to a_4, and in some compounds (5-methyl, 8-methyl, 9-methyl, 10-methyl, and 1′,10-dimethyl) band a_5 can also be decerned as an inflection on the leading edge of band λ.

Considerable interest is attached to the band of lowest frequency, which we have identified as a_0. This has theoretical implications that are considered in the discussion section.

The spacing of the a_0 band from the a_1 band lies in the range 1425±65 cm.$^{-1}$ in all except the 10-methyl compound. In the 10-methyl spectrum, the band of lowest frequency is at 25,720 cm.$^{-1}$, spaced 1130 cm.$^{-1}$ below the band at 26,850 cm.$^{-1}$ which we must assign to a_1 by virtue of its relationship to the higher members of the *a* series. The 25,720 cm.$^{-1}$ band is consistent with a β assignment and is spaced 1380 cm.$^{-1}$ below the inflection at 27,100 cm.$^{-1}$ which is assigned to δ (Fig. 10). The difficulty associated with the assignment of the a_0 band in 10-methyl-1,2-benzanthracene is important theoretically and it cannot be due solely to the presence of the 10-methyl substituent since in the 1′,10-dimethyl compound the band of lowest frequency (a_0) is at 25,530 cm.$^{-1}$, spaced 1360 cm.$^{-1}$ below a_1. From this we must conclude either that band a_0 is absent from the spectrum of the 10-methyl compound, or else that the a_1–a_0 spacing of 1425±65 cm.$^{-1}$ is fortuitous in its seeming relationship to the

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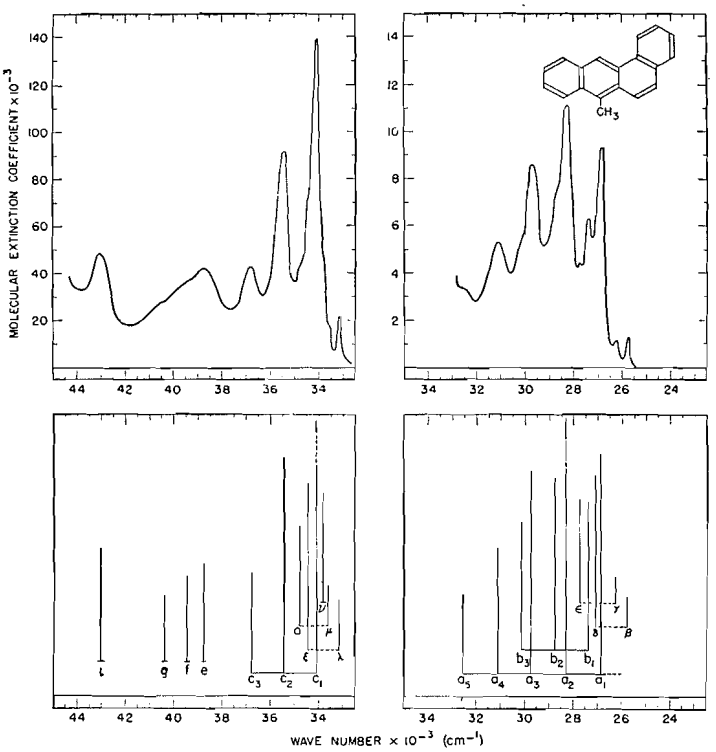

FIG. 10. Ultraviolet absorption spectrum of 10-methyl-1,2-benzanthracene in *n*-pentane solution at −100°C.

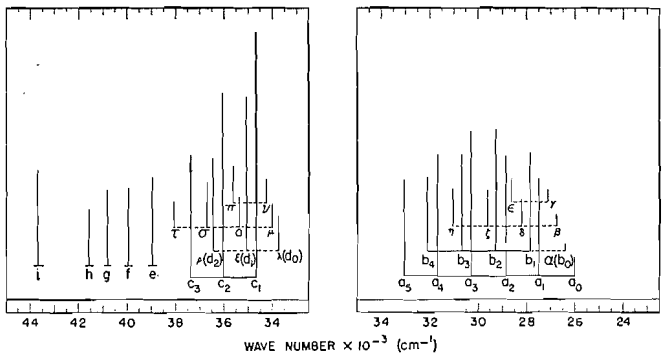

FIG. 11. Schematic diagram of proposed absorption band systems generalized from the spectra of 1,2-benzanthracene and all methyl derivatives.

1408±90 cm.$^{-1}$ spacing between the higher members of the *a* series in all the other 18 derivatives.

The first member of the *b* series that can be clearly recognized in all the compounds is located between a_1 and a_2, and is defined as b_1. A weak band (α) is observed near b_1-1400 cm.$^{-1}$ in the spectrum of 1,2-benzanthracene and in the 2′-methyl, 4-methyl, 6-methyl, and 2′,7-dimethyl compounds; the b_1–β

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spacing is also approximately 1400 cm.$^{-1}$ in the 1′-methyl, 3-methyl, and 7-methyl compounds. These might suggest that there is a weak b_0 member of the series, but no band assignable to b_0 can be observed in the spectra of the other compounds. The mean spacings for the b_4, b_3, b_2, b_1 series in all the compounds is 1423±85 cm.$^{-1}$, but the difference from the a series spacing of 1408±90 cm.$^{-1}$ is not considered significant.

With diminishing temperature, both the a and b series sharpen, but the temperature effect is usually much more pronounced on the a series than on the b series, as is shown for the 4-methyl compound in Fig. 12.

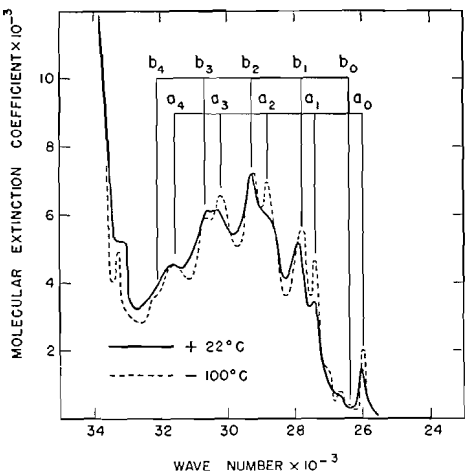

FIG. 12. Ultraviolet absorption spectrum of 4-methyl-1,2-benzanthracene in n-pentane solution illustrating differential temperature effects on the a and b band series.

The α–η Bands

The letters $\alpha \ldots \eta$ are assigned to weak bands or inflections that overlap the a and b series. These bands show positional analogies in the various compounds from which it might be inferred that the bands carrying the same letter are probably associated with similar excitation processes in the different compounds; there is however no real evidence for this.

In several of the compounds it has been noted above that α might be associated with the b series. In all 11 compounds where δ is observed, the δ–β spacing falls in the range 1383±150 cm.$^{-1}$. In the 8-methyl compound two additional inflections are also observed with spacings η–ζ, ζ–δ, and δ–β of 1400, 1260, and 1250 cm.$^{-1}$. Some of the other compounds show changes of contour on the sides of the a_2 and a_3 bands which suggest that bands analogous to η and ζ might be detected under more favorable experimental conditions (e.g. lower temperatures). These bands probably result from combination of the a series excitations with other vibrational modes.

The bands ϵ and γ are observed in four compounds and band γ alone in an additional six. These are weaker and more diffuse than the η, ζ, δ, β series, but probably arise from a similar type of excitation process.

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The c Series

Between 38,000 and 33,000 cm.$^{-1}$ the spectrum is dominated by the c series, and in all compounds three members of this series are observed with spacings of 1373±105 cm.$^{-1}$. This is considered a significantly smaller spacing than that noted above for the a and b series. Bands e and f are observed in the region where c_4 and c_5 would be expected. In the 4-methyl, 5-methyl, and 9-methyl compounds the positions and intensities of e and f are not inconsistent with c_4 and c_5 assignments, but in the other compounds neither the positions nor the intensities of bands $e \ldots h$ can be reconciled with the extension of the c series beyond c_3.

The λ–τ Bands

The fine structure that appears between a_5 and c_3 shows a similarity to the fine structure of the $\alpha \ldots \eta$ group, but there is a suggestion that bands λ, ξ, and ρ which have a mean spacing of 1346 cm.$^{-1}$±140 cm.$^{-1}$ may constitute a d series. They are, however, too strongly overlapped by the c series to establish this with certainty.

The c series is much more temperature sensitive than the underlying bands, and this is particularly noticeable on c_1. Attempts have been made in earlier work to associate the position of the peak of the absorption envelope in this region ("band D" of Fig. 1) with the relative carcinogenicity of these compounds (11). We see from the present series of measurements that this peak is composite, and the position of this maximum is more sensitive to temperature change than other parts of the absorption envelope. In a number of cases (such as the 6-methyl compound, shown in Fig. 13), the contour of the band envelope

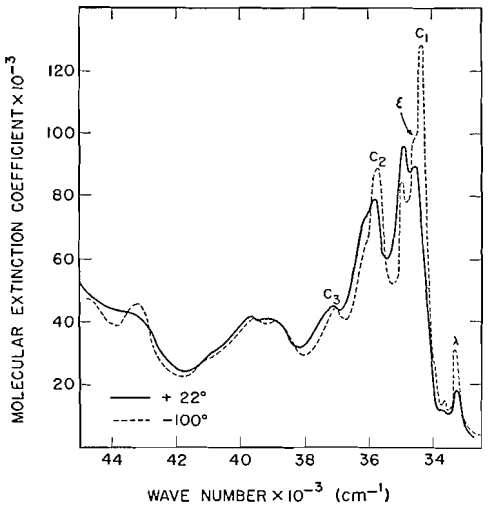

FIG. 13. Ultraviolet absorption spectrum of 6-methyl-1,2-benzanthracene in n-pentane solution illustrating strong temperature effect in the neighborhood of band C_1.

suggests that at room temperature band ξ predominates and that the relative intensities of the ξ and c_1 peaks are reversed on cooling.

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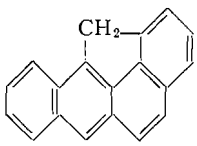
Absorption above 38,000 cm.$^{-1}$

In all the compounds there is a well-defined band near 43,000 cm.$^{-1}$ (band *i*), and this constitutes the upper limit of our range of measurement. The group of three or four bands (*h* . . . *e*) between 42,000 and 38,000 cm.$^{-1}$ is usually very diffuse.

The Spectrum of 1′,9-Methylene-1,2-benzanthracene

It has been noted previously (12) that the spectra of 1′,9-methylene-1,2-benzanthracene (II) and its 10-methyl derivative differ significantly from the spectra of the simple alkyl 1,2-benzanthracenes. The low temperature spectrum



II

of II is shown in Fig. 14. The main differences are noted between 36,000 and 34,000 cm.$^{-1}$ and between 28,000 and 25,000 cm.$^{-1}$. The region below 33,000

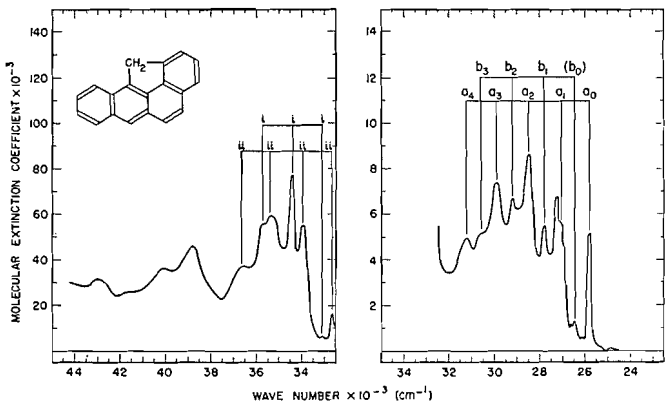


FIG. 14. Ultraviolet absorption spectrum of 1′,9-methylene-1,2-benzanthracene in *n*-pentane solution at −100°C.

cm.$^{-1}$ consists of two well-defined series of bands, the stronger of which we can identify with our *a* series, and the weaker with our *b* series. The *a* series seems more pronounced than in the simple alkyl derivatives. The spectrum between 38,000 and 32,000 cm.$^{-1}$ can also be resolved into two series of bands (*i* and *ii*). It is not clear what relationship these two series bear to the *c* and (tentative) *d* series of the methyl derivatives.

DISCUSSION

The principle features of the near ultraviolet spectra of aromatic hydrocarbons have been discussed by Coulson (5) and by Klevens and Platt (18, 25, 26). These authors developed molecular orbital treatments of the electronic energy levels of these molecules, which Moffitt (24) has refined and extended.

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In benzene, the three lowest singlet electronic band systems begin near 38,000, 48,050, and 57,000 cm.$^{-1}$. These are associated with excitation from the ground state (^1A) to the L_b, L_a, and B_b excited states of Platt. They correspond to the α, p, and β bands of Clar.* The first two of these electronic transitions are forbidden by symmetry and appear only in combination with non totally symmetrical vibrations.

The near ultraviolet and visible spectra of the acene polynuclear aromatic hydrocarbons also exhibit three broadly distinguishable band systems, and these are generally considered to be related to the three electronic states of benzene described above. The band of lowest frequency (Clar's α band) is polarized along the longer in-plane axis, as is required for the ^1A–^1L_b transition. The next band system (Clar's p band) is polarized along the shorter in-plane axis, while the third band series (Clar's β) is again long-axis polarized. The p-system was first shown by Clar to be very sensitive to linear "Anellierung" and to shift rapidly to lower frequency in the series naphthalene → anthracene → naphthacene → pentacene. Clar's α band is much less affected by linear "Anellierung". In anthracene and naphthacene it is submerged beneath the stronger and more rapidly moving p-system (p. 249 of Ref. 3). Clar's strong β band increases in intensity with linear "Anellierung" and shifts to lower frequency at about the same rate as the α band.

In the angular acene hydrocarbons the same three groups of bands are identified. Clar's α and β bands remain in approximately the same positions as in the linear "anellierte" isomers, but the p band is displaced to higher frequency. Platt has described these bands in terms of "long field" and "round field" structures (26), and has shown in a few cases that, as the two principle in-plane axes become more similar, the p band system shifts to higher frequency.

The above description has been concerned only with the electronic transitions, and the quantum mechanical treatments of Coulson, Platt, and Moffitt do not take notice of the vibrational structure. This vibrational structure is associated mainly with 0–0, 0–1, 0–2 . . . transitions in accordance with selection rules developed by Herzberg, Sponer, and Teller (10, 28). This vibrational structure has been investigated more thoroughly for naphthalene than for the more complex polynuclear aromatic hydrocarbons (15, 20, 21, 22, 27). The spacing of approximately 1400 cm.$^{-1}$ to which we attach particular importance in our analyses of the 1,2-benzanthracene spectra is common to many polynuclear aromatic hydrocarbons and shows up prominently in anthracene (12).

If we disregard the minor bands, we have in 1,2-benzanthracene the three well-established a, b, and c series which are all progressions of a 1400 cm.$^{-1}$ vibration. Our a series might be identified with Platt's A–L_b transition and our b series with Platt's A–L_a transition. In both the L_b and L_a states the equilibrium positions of the atoms must be significantly different from those in the ground state, as the most intense bands are about the middle of the progres-

**For purely descriptive purposes we prefer to use Clar's nomenclature since it avoids implications concerning the type of electronic transition involved.*

sion. No "hot" bands arising from excited vibrational levels of the ground state would appear to be present since we see no bands that weaken on cooling.

This interpretation would imply that the *a* and *b* band series are associated with excitation to closely lying but distinct electronic states, rather than to two different vibrations and their overtones in the same excited state. Our experimental observations do not allow us to distinguish with certainty between these alternative interpretations, but there are two arguments that favor the hypothesis of separate electronic states. If only one electronic state were involved we would formulate the *a* series as

$$a_n = a_0 + 1400\,n \qquad (n = 0, 1, 2, 3, 4, 5) \qquad [2]$$

and the *b* series

$$b_n = a_0 + \nu_b + 1400\,n \qquad [3]$$

where ν_b is a vibrational term that combines with the $1400\,n$ term. A comparison of the frequencies of the individual *a* and *b* bands in the complete series of compounds (Table II) shows that the spacing between the two series $(b_n - a_n)$ varies over a range from 774 cm.$^{-1}$ for the 2′,7-dimethyl compound to 200 cm.$^{-1}$ for the 6-methyl compound, and it seems unlikely that a combination term such as ν_b of equation [3] would behave in this manner. The inverse of this argument has been used by McConnell and McClure (21) to support their contention that part of the fine structure in the naphthalene spectrum involves only one electronic state. The marked difference in the temperature effect on the *a* and *b* band series is also more readily explained in terms of two separate electronic states, as this type of behavior would hardly

TABLE II

MEAN SEPARATION $(b_n - a_n)$ BETWEEN BANDS OF THE *b* SERIES AND *a* SERIES IN THE ULTRAVIOLET ABSORPTION SPECTRA OF 1,2-BENZANTHRACENES

Compound	$(b_n - a_n)$, cm.$^{-1}$
1,2-Benzanthracene	346
1′-Methyl-1,2-benzanthracene	502
2′-Methyl-1,2-benzanthracene	502
3′-Methyl-1,2-benzanthracene	235
4′-Methyl-1,2-benzanthracene	210
3-Methyl-1,2-benzanthracene	674
4-Methyl-1,2-benzanthracene	424
5-Methyl-1,2-benzanthracene	363
6-Methyl-1,2-benzanthracene	200
7-Methyl-1,2-benzanthracene	610
8-Methyl-1,2-benzanthracene	287
9-Methyl-1,2-benzanthracene	365
10-Methyl-1,2-benzanthracene	497
1′,10-Dimethyl-1,2-benzanthracene	290
2′,6-Dimethyl-1,2-benzanthracene	412
2′,7-Dimethyl-1,2-benzanthracene	774
3′,6-Dimethyl-1,2-benzanthracene	300
3′,7-Dimethyl-1,2-benzanthracene	390
9,10-Dimethyl-1,2-benzanthracene	—
1′,9-Methylene-1,2-benzanthracene	690

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be expected for two vibrations of closely lying frequency in the same electronic level.

These observations would also be compatible with the assumption of the excitation of one of the series from an excited level lying very near the ground state. Such a postulation of two closely lying initial states, however, would seem unlikely on chemical grounds for a molecule of this type.

In the 38,000–33,000 cm.$^{-1}$ region we can associate the c band series with the A–B_b electronic transition of Platt, and there is no reason to question the assignment of the intense c_1 band to the 0–0 vibrational transition, since we can detect no band near c_1-1400 cm.$^{-1}$. In the B_b state the equilibrium positions of the atoms would be similar to those in the ground state if the 0–0 band is the most intense. If we accept the more problematical identification of bands λ, ξ, and ρ with a d series we are presented with a problem of interpretation very similar to that of the a and b series discussed above, and we would then require four electronic transitions to account for the observed spectrum below 38,000 cm.$^{-1}$; this is one more than is provided by the theoretical treatments of Platt and of Moffitt. We might note in this connection that neither of these authors made any assignment for our band λ which we would now regard as the 0–0 vibrational transition associated with a postulated fourth electronic state. In the above discussion we have omitted consideration of the minor bands μ, ν, o, π, σ, τ, but these probably arise from other combinations of vibrational terms.

Above 38,000 cm.$^{-1}$ these studies do not add greatly to our knowledge of these spectra. They suggest only that the absorption above 38,000 cm.$^{-1}$ is not directly related to that below, and we may therefore need to invoke one or more additional electronic states to account for bands e, f, g, h, and i. Band i has been associated by Platt with his ^1A–^1C_b transition.

We have noted in a previous section that in 10-methyl-1,2-benzanthracene there are difficulties in assigning the a_0 band. If we accept this as evidence that the numerical relationship of the a_0 band to the higher members of the a series is fortuitous in all the other compounds, we have to conclude that a_0 forms a separate band system. This is contradicted however by the general observation that in those compounds in which a_0 is prominent the same holds true also for the other bands assigned to the a series. This can be noted by comparison of the spectra of the 2′-methyl and 1′,9-methylene compounds on the one hand with that of the 6-methyl on the other (Figs. 8, 9, 14).

In view of the high intensity of all of this absorption we must presume that it arises from singlet–singlet transitions, and McClure (20) has identified the first and second singlet–triplet transitions of 1,2-benzanthracene with much weaker absorption near 16,500 and 35,950 cm.$^{-1}$.

CONCLUDING REMARKS

It will be of interest to determine whether or not the spectra of other types of polynuclear aromatic hydrocarbons can be treated in a similar fashion. In this connection we would stress the value of examining an extensive set of simple alkyl derivatives. The diffuseness of the bands, even at low temperatures,

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makes it difficult to locate the positions of the maxima with sufficient precision to establish the validity of such series from observations on a single compound. Alkylation appears to have a definite effect in displacing the series relative to each other, and it is only when similar series of bands can be identified in the spectra of a number of alkyl derivatives that we consider these conclusions to have significance. Similar studies are at present being made on the methyl-3,4-benzphenanthrenes and will be reported in due course.

It may be noted in conclusion that attempts have been made to correlate the bathochromic shifts produced by methylation with the conjugating power defined in terms of the self-polarizability of 1,2-benzanthracene at the position of substitution (1). More recently the electron density in the highest occupied orbital has been employed (24*a*). The correlations between these calculated shifts and the observed shifts are often far from satisfactory. The observed shifts are determined from the maxima of the band envelopes; the present work emphasizes the complexity of these band envelopes and the sensitivity of their peak positions to extraneous influences. It is therefore not surprising that the agreement between theory and experiment is relatively poor.

ACKNOWLEDGMENTS

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THE PREPARATION AND PROPERTIES OF α-D-GLUCOPYRANOSE 1,2-(ETHYL ORTHOACETATE) TRIACETATE[1]

By R. U. Lemieux and J. D. T. Cipera[2]

ABSTRACT

Crystalline ethyl and propyl 1,2-orthoacetates of α-D-glucopyranose triacetate were prepared. Conclusions are drawn regarding the chemical properties and configurations of these compounds which are based on the conformation of the 1,2-cyclic carboxonium ion believed to be formed when the substances are treated with acetic acid.

Lemieux and Brice (10) prepared a crude sirupy α-D-glucopyranose 1,2-(methyl orthoacetate) triacetate by reaction of tetra-*O*-acetyl-β-D-glucopyranosyl chloride (I) with methanol in the presence of silver carbonate. We wish to report crystalline ethyl (III) and *n*-propyl 1,2-orthoacetates of α-D-glucopyranose triacetate obtained by reaction of the β-chloride (I) with the appropriate alcohol in the presence of dry pyridine. The orthoesters crystallized directly from the reaction mixture and are thus readily prepared. All efforts to obtain crystalline α-D-glucopyranose 1,2-(methyl orthoacetate) triacetate have failed.

The compound III in the presence of acids and bases reacted in the manner expected for orthoacetate structures (12). In view of the established properties of the β-chloride (I) (10) and related compounds (7), there could be little doubt that the substance possesses a 1,2-orthoacetate ring. This prediction was confirmed by deacetylation of III followed by methylation and hydrolysis of the product to form 3,4,6-trimethyl-D-glucose. It is noteworthy that these reactions provide a much easier preparation of the latter compound than was hitherto available (13).

The orthoester (III) had a half-life of 4.38 min. (polarimetric) when dissolved in 95% aqueous dioxane 0.0061 *N* with hydrochloric acid at 28°C. When the compound was dissolved in 99% acetic at 28°C. it was rapidly (1.75 min.) converted to 2,3,4,6-tetra-*O*-acetyl-α-D-glucose (V). However, in carefully dried acetic acid, β-D-glucopyranose pentaacetate (VI) was the main product. Thus, the behavior of the orthoester in acetic acid paralleled closely that of the β-chloride (I) in wet and dry acetic acid (10). When the orthoester (III) was dissolved in acetic acid containing varying amounts of water, the rotation of the reaction product increased with increasing amounts of water until the amount of water was about equimolar to the orthoester. Greater amounts of water resulted in reaction products with approximately the same rotation (see Table I). Thus, the orthoester reacted substantially quantitatively with the traces of water present in the acetic acid. This result strongly suggests that the orthoester (III) is dissociated in acetic acid to the cyclic carboxonium

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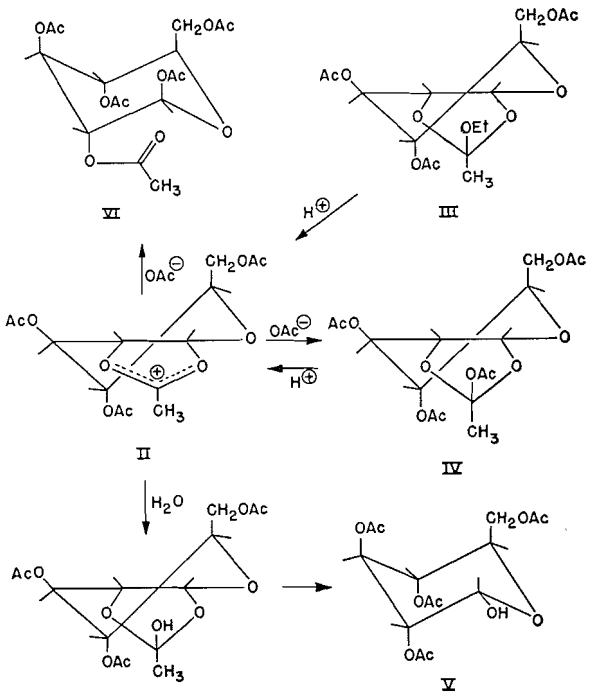
TABLE I

MAXIMUM ROTATION ACHIEVED IN THE REACTION OF α-D-GLUCOPYRANOSE 1,2-(ETHYL ORTHOACETATE) TRIACETATE (0.089 *M*) IN AQUEOUS ACETIC ACID

Concentration of water (*M*)[a]	Specific rotation
0	+51°[b]
0.041	77
0.062	99
0.19	103
0.53	107

[a]*See the experimental portion.*
[b]*The specific rotation of β-glucopyranose pentaacetate under these conditions was 5.5°.*

ion (II) through co-ordination of the acid with the ethoxyl group oxygen atom rather than by co-ordination with the central atom of the C_5–O–C_1–O–C–O–C_2 system as proposed by Pacsu (12, p. 103) for acid hydrolysis of cyclic sugar orthoesters. The result strongly infers this reaction route because of the stereochemical results of the hydrolysis and acetolysis reactions and the fact that the ion (II) can be expected to accept a nucleophilic reagent at the easily accessible 1,2-cyclic structure much more readily than at the highly hindered (because of the axial CH_2OAc group) rear side of the lactol carbon atom. Thus, the ability of the ion to search out mere traces of water in acetic acid becomes understandable. The 1,2-(acetyl orthoacetate) triacetate (IV) must have a



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transient existence in these reactions. Furthermore, reaction by way of the ion (II) is highly attractive from energy considerations (7). The conformation of the ion (II) is based on the established conformation of six-membered rings fused 1,2-*cis* to planar five-membered ring (1, 4) and on the evidence provided by Lemieux and Brice (9) that the CH_2OAc group must be situated in close proximity to the anomeric center.

It has often been observed in the preparation of sugar 1,2-orthoesters that the degree of partial asymmetric synthesis is high since only one of the two possible diastereoisomers is obtained and this often in high yield. A consideration of a molecular model of the ion (II) leaves little doubt that the orthoester (III) is formed by approach of the nucleophilic reagent on the side of the positively charged center which is *trans* to the pyranose ring. The orthoester (III) must possess the α-D-configuration and has a much lower specific rotation, +31°, than has ethyl α-D-glucopyranoside tetraacetate, +132.1° (5). On the other hand, β-D-mannopyranose 1,2-(methyl orthoacetate) triacetate has a specific rotation, −26.6° (3), not greatly different from that of methyl β-D-mannopyranoside tetraacetate, −46.8° (3). Clearly, therefore, the difference in rotation cannot be attributed to contributions to rotation by the asymmetric center of the orthoester group. Instead, these data strongly suggest that conformation has an important effect on rotation. It is of interest to note in this respect that the rotation of the orthoester (III) is close in value to that measured for 1,2-(1-methylpentylidene)-α-D-glucopyranose triacetate, +24.7°, by Hurd and Holysz (6).

EXPERIMENTAL

β-D-*Glucopyranosyl Chloride Tetraacetate* (*I*)

The material used, m.p. 95–98°C., was prepared by the procedure of Lemieux and Brice (10) and was recrystallized once from ether–pentane.

α-D-*Glucopyranose 1,2-*(*Ethyl Orthoacetate*) *Triacetate* (*III*)

The chloride (I), 6 gm., was added to a mixture of 3 ml. dry pyridine in 15 ml. anhydrous ethanol. The compound (II) dissolved after the mixture was shaken at room temperature for 20 min. The mixture was left at −10°C. for 30 hr. and the crystalline product was collected. After two recrystallizations from ethanol, the yield was 3.96 gm. (61.5%), m.p. 97–97.5°C., $[\alpha]_D$ +31° (*c*, 1 in chloroform). These constants were not changed by further recrystallizations. Calc. for $C_{16}H_{24}O_{10}$: C, 51.1; H, 6.42%; saponification equiv., 125.4. Found: C, 50.3; H, 6.1%; saponification equiv., 125.5, 124.8. The half-time of reaction, determined polarimetrically, was about 14.5 min. when 100 mgm. of the chloride (I) was dissolved in 5 ml. of 9:1 ethanol–pyridine at room temperature.

The results given in Table I for the reactions of the ethyl orthoester (III) in acetic acid solution were obtained by dissolving 100 mgm. of the compound in 3 ml. of the acetic acid. The dry acetic acid was prepared by reacting glacial acetic acid with acetic anhydride in the presence of sulphuric acid followed by distillation in a dry atmosphere. The solutions of water in acetic

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acid were prepared gravimetrically. Since the specific rotation of the β-D-glucopyranose pentaacetate in this solvent was +5.5° and the reaction of the ethyl orthoester in the solvent gave a rise in rotation to +51°C., it was apparent that either the acetic acid was not altogether dry or else some water was absorbed in the several transfers necessary to prepare the solution and to follow the rotation. It was clear that the latter was the case since substantially pure β-D-glucose pentaacetate, m.p. 129–132°C. (pure, m.p. 132.5–133.5°C. after one recrystallization from ethanol), was formed when the ethyl orthoester (III) was dissolved in the solvent kept in a dry atmosphere. When the orthoester (III), 100 mgm., was dissolved in 6 ml. of 99% acetic acid, the product was soluble and mutarotated in water. Recrystallization of the material from ether–pentane gave 2,3,4,6-tetra-*O*-acetyl-α-D-glucose (10), m.p. 97.5–98.7°C., $[\alpha]_D$ +122° (chloroform).

*3,4,6-Tri-O-methyl-*D*-glucose*

The ethyl orthoester (III), 1.1 gm., was deacetylated at room temperature with methanolic ammonia. The sirup, which remained after solvent removal, was dissolved in 2 ml. dry methanol and the solution was methylated with 6 ml. methyl iodide and 6 gm. silver oxide added in portions in the usual manner (2). The product was remethylated in the same manner except that only 0.5 ml. of methanol was used. The product was extracted with hexane to yield a hexane-soluble sirup which gave an observed rotation +10° in 5 ml. dioxane. The rotation rapidly rose to +24° on the addition of 0.25 ml. of 0.1 *N* hydrochloric acid. The orthoester ring therefore survived the methylation. The solution was evaporated to dryness and the residue was heated at 100°C. for two hours with 10 ml. 0.1 *N* hydrochloric acid to complete hydrolysis. Paper chromatography showed the solution to contain a substance with the R_f value in the range expected for a trimethylglucose along with a small amount of dimethylglucose. The dimethyl derivative was removed by partition chromatography using Celite to support the aqueous phase and *n*-butanol saturated with water as the developing phase (11) to yield 360 mgm. of trimethylglucose. This substance must be 3,4,6-trimethyl-D-glucose, since it was rapidly and completely converted by periodate to only one substance which after alkaline hydrolysis moved on a paper chromatogram in the manner expected for 2,3,5-tri-*O*-methylarabinose (8).

α-D-*Glucopyranose 1,2-(n-Propyl Orthoacetate) Triacetate*

This substance was obtained in 62% crude yield, m.p. 60–69°, under the conditions described above for the preparation of the ethyl orthoester. Two recrystallizations from ethanol gave apparently pure material, m.p. 92–94.5°C., $[\alpha]_D$ +39.5° (*c*, 1 in chloroform). The substance possessed the properties expected for an orthoester structure and must be the compound indicated.

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A NEW SYNTHESIS OF DL-γ-HYDROXY-ORNITHINE[1,2]

By Guy Talbot, Roger Gaudry, and Louis Berlinguet

ABSTRACT

A convenient synthesis of DL-hydroxy-ornithine is described. Starting from diethyl allylmalonate, it involves treatment with sulphuryl chloride followed by hydrolysis and distillation to give a 90% yield of 2,5-dichloro-4-valerolactone. Condensation of this with two equivalents of potassium phthalimide in dimethylformamide gives a quantitative yield of crude 2,5-diphthalimido-4-valerolactone. This lactone is converted quantitatively by acid hydrolysis to DL-γ-hydroxy-ornithine, isolated as the dihydrochloride of the corresponding 2,5-diamino-4-valerolactone. The over-all yield calculated from allyl chloride is 80%.

INTRODUCTION

2,5-Diamino-4-hydroxyvaleric acid (hydroxy-ornithine), a "non-natural" amino acid, was first synthesized in 1916 by Hammarsten (8), starting from allylhippuric acid. Other syntheses, developed by Traube, Johow, and Tepohl (13) in 1923, involved condensation between epichlorhydrin and diethyl malonate. In 1926, Tomita and Fukagawa (11) condensed 1-chloro-2-hydroxy-3-phthalimidopropane with diethyl phthalimidomalonate and in 1935, Tomita and Nakashima (12) reported on similar compounds. An attempt to synthesize hydroxy-ornithine from histidine by Langenbeck and Hutschenreuter (9) in 1929 has proved to be unsuccessful. Finally, Dey (3), in 1937, published a synthesis in which 1,2-epoxy-3-phthalimidopropane was condensed with diethyl malonate.

However, these various condensations led to extremely low yields of hydroxy-ornithine and consequently are not suitable for the preparation of substantial quantities of this amino acid. The need for a readily available intermediate thus became obvious.

The 2,5-dichloro- or 2,5-dibromo-valerolactones, which can be readily obtained (5), were first considered as possible starting materials. However, treatment of these lactones with ammonia favored cyclization to hydroxy-proline (5).

It was therefore decided to investigate the condensation of these 2,5-dihalogenated-4-valerolactones with potassium phthalimide.

Diethyl allylmalonate (III) was prepared in a 91% yield by condensation of allyl chloride (I) and diethyl malonate (II). Treatment of diethyl allylmalonate (III) with sulphuryl chloride or addition and substitution of bromine to the unsaturated free acid (IV) in chloroform, followed in both cases by acid hydrolysis and vacuum distillation, gave respectively a 90% yield of the 2,5-dichloro-4-valerolactone (V) and a 73% yield of the dibromo derivative (VI) (based on

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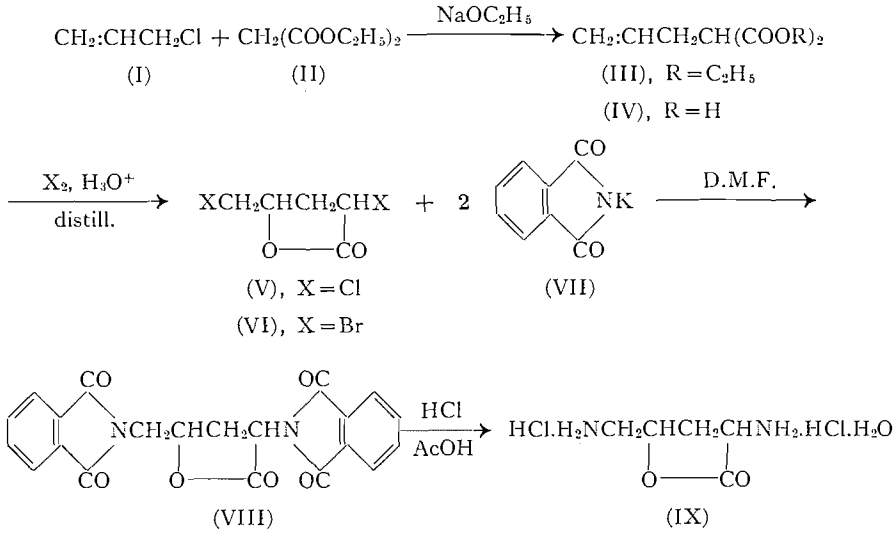
Contribution from the Department of Biochemistry, Faculty of Medicine, Laval University, Quebec, Que.
[2]*Paper presented before the Division of Chemistry at the 22nd Meeting of the Association Canadienne-Française pour l'Avancement des Sciences (A.C.F.A.S.), Quebec, Que., November 6, 1954.*

allylmalonic acid, itself obtainable in 82% yield by saponification of the corresponding diester).



The next step involved condensation of the dihalogenated lactones with two equivalents of potassium phthalimide (VII). Dimethylformamide (D.M.F.) was successfully used as a solvent for this reaction while other solvents like toluene or xylene (7) did not lead to a homogeneous product. In this manner, the two lactones led to a quantitative yield of crude 2,5-diphthalimido-4-valerolactone (VIII) which is virtually insoluble and which was best purified with little lost by treatment with activated charcoal in a large volume of glacial acetic acid.

The hydrolysis of the 2,5-diphthalimido-4-valerolactone (VIII) with a mixture of glacial acetic acid and concentrated hydrochloric acid gave a nearly quantitative yield of hydroxy-ornithine isolated as 2,5-diamino-4-valerolactone dihydrochloride monohydrate (IX).

The over-all yield of hydroxy-ornithine through the dichlorolactone amounted to 80% based on allyl chloride.

EXPERIMENTAL*

Diethyl Allylmalonate (III)

Using the method of Conrad and Bischoff (2), 153 gm. of allyl chloride (I) and 641 gm. of diethyl malonate (II) were condensed to give diethyl allylmalonate (III). Yield: 364 gm. (91%), b.p. 71–73° (1.5 mm.), n_D^{20}: 1.430. (Lit.: b.p. 93° (6 mm.) (4), n_D: 1.433 (6) or n_D^{20}: 1.430 (7).)

2,5-Dichloro-4-valerolactone (V)

Diethyl allylmalonate (III) (169.3 gm.) was treated with sulphuryl chloride (243 gm.), then hydrolyzed and vacuum distilled to give 2,5-dichloro-4-

**Melting points are uncorrected.*

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valerolactone (V) as described by Gaudry and Godin (5). Yield: 129.1 gm. (90.5%), b.p. 118–121° (2 mm.), n_D^{20}: 1.495. (Lit.: b.p. 159–161° (13 mm.) (10), $n_D^{24.6}$: 1.496 (1).) Anal. Calc. for $C_5H_6O_2Cl_2$: Cl, 42.0. Found: Cl, 41.6.

Allylmalonic Acid (IV)

Saponification of 100 gm. of diethyl allylmalonate (III) by sodium hydroxide, followed by acidification, gave allylmalonic acid (IV). Yield: 58.8 gm. (82%), m.p. 103°. (Lit.: m.p. 103° (2).)

2,5-Dibromo-4-valerolactone (VI)

Allylmalonic acid (IV) (58.8 gm.) was treated with bromine (163 gm.) as described by Gaudry and Godin (5). The yield of 2,5-dibromo-4-valerolactone (VI) was 83.3 gm. (73%), b.p. 156–157° (4 mm.), n_D^{20}: 1.557. (Lit.: b.p. 150–151° (3 mm.), n_D^{20}: 1.555 (7).) Anal. Calc. for $C_5H_6O_2Br_2$: Br, 62.0. Found: Br, 62.1.

2,5-Diphthalimido-4-valerolactone (VIII)

2,5-Dichloro-4-valerolactone (V) (106.9 gm., 0.63 mole) was added dropwise, at room temperature, to a mechanically stirred suspension of potassium phthalimide (VII) (262 gm., 1.41 moles) in dimethylformamide (800 ml.). The mixture was then heated to about 100° for six hours. The liquid was slowly poured into four liters of water with vigorous stirring, the cold suspension filtered, and the residue washed thoroughly with water–ethanol mixture (4:1) and dried at 105° for several hours. The amorphous material thus obtained was sufficiently pure for use in the next step. Yield of crude product: 252 gm. Recrystallization from a large volume of glacial acetic acid gave crystals, m.p. 263°. (Lit.: m.p. 260° (3).) Anal. Calc. for $C_{21}H_{14}N_2O_6$: N, 7.18. Found: N, 7.24.

2,5-Diamino-4-valerolactone Dihydrochloride Monohydrate (IX)

A mixture of glacial acetic acid (350 ml.), concentrated hydrochloric acid (700 ml.), and 2,5-diphthalimido-4-valerolactone (VIII) (70.0 gm., 0.18 mole) was heated under reflux for 24 hr. The rather insoluble compound dissolved gradually as the hydrolysis proceeded. The filtrate was evaporated to dryness under reduced pressure after the phthalic acid had been removed from the cold solution. The residue was dissolved in water and the solution was decolorized with Norit, concentrated to a small volume, and precipitated by the addition of ethanol. Recrystallization from water–ethanol mixture gave the monohydrate of the 2,5-diamino-4-valerolactone dihydrochloride (IX). Yield: 38.8 gm. (98%), m.p. 239°. (Lit.: m.p. 239–240° (13).) Anal. Calc. for $C_5H_{10}O_2N_2.2HCl.H_2O$: N, 12.68; Cl, 32.05. Found: N, 12.68; Cl, 31.80.

The dihydrochloride when filtered through a column of a strongly basic resin (Permutit S-1) apparently gave the monohydrochloride, which could not be isolated. However, a chloride determination on an aliquot from the eluate gave a figure roughly equivalent to one half of the total chloride content of the dihydrochloride. The monopicrate, obtained by treating the eluate with one equivalent of picric acid, had a sharp melting point of 180° instead of 185–190° as reported by Hammarsten (8).

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The 2,5-diamino-4-valerolactone, being a weak base, migrated toward the cathode when submitted to paper electrophoresis in a buffer solution of pH 8.6. The 2,5-diamino-4-valerolactone had a R_f value of about 0.24 on circular chromatograms in 80% pyridine – 20% water system, while in phenol saturated with water the R_f value for a one-dimensional chromatogram was around 0.10.

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THE POTENTIOMETRIC METHOD FOR THE DETERMINATION OF ALUMINUM ON A SEMIMICRO SCALE[1]

By J. R. McCallum[2]

ABSTRACT

The potentiometric method for the determination of aluminum proposed by Treadwell and Bernasconi has been modified for use on a semimicro scale and applied successfully to the analysis of pulp and paper ash. Samples containing as little as one milligram of aluminum have been titrated with an accuracy of 0.003 milligrams or better.

INTRODUCTION

A description of a potentiometric method for the determination of aluminum by titration with sodium fluoride, using a ferri-ferrous half cell, first appeared in a paper by Treadwell and Bernasconi (32) in 1930. The technique described in this paper is essentially the same as the original method except that it has been revised in detail to enable the determination to be made on the semimicro scale.

There are no other references to the practical application of this method in the West-European or North-American literature, except in such review papers as those by Furman (12, 13) and in the textbook by Kolthoff and Furman (17). In Eastern Europe the technique has proved to be popular and valuable for analysis of samples containing 50 mgm. or more of aluminum oxide. For example, Stefanovskii and Svirenko (23) applied the method to silicates and other ores with much success. They found that the method was not of much value for ores giving an iron oxide precipitate four or five times heavier than the aluminum oxide present. Ivanov and Bezyaiko (16) adopted the method for the determination of aluminum in steel and found it very useful if a partial separation of the iron from the aluminum was performed before the titration. This technique could also be applied to the ores high in iron content. These latter authors also found the method to be useful in the analysis of bronze. Mannchen (19) used the method for the determination of aluminum in magnesium alloys, and Pollack (20) used it in connection with electron-type alloys.

The versatility of this titration is not limited to the determination of aluminum in the presence of iron for widely differing samples. Suitably modified it has been used with great success to determine fluorine, titrating with an aluminum salt (25, 26), ferric chloride (24), or cerous nitrate (21). Dubinkov and Tikhomirov (11) compared several methods of fluorine analysis and found that the potentiometric titration was accurate for the analysis of sample solutions containing 0.2 mgm. of fluorine per liter or more. Tarayan (27) titrated beryllium in the absence of aluminum and calcium in the absence of magnesium (28) while Ringbom and Merikanto (22) also found it possible to determine calcium in this way.

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Contribution from the Quebec North Shore Paper Company, Baie Comeau Mill, Baie Comeau, Que.
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The method has a very firm theoretical foundation due almost entirely to the monumental work of Brosset and co-workers in Stockholm (Refs. 2 to 8). Contributions to the knowledge of the fundamental chemistry of the ferri-ferrous half cell and of the fluorine complexes formed during this titration have also been made by such authors as Connick and Tsao (9), Dodgen and Rollefson (10), Low and Pryde (18), and Babko and Kleiner (1). These papers are for the most part written in English and are readily obtainable so that a discussion of this theory is not necessary here.

During certain studies on pulp and paper it became necessary to analyze rapidly small samples of ash for various cations including aluminum. Several methods were attempted but all except this potentiometric procedure were unsuitable. For example, the classical methods of separation are accurate enough for fairly large amounts of aluminum but on the semimicro scale errors of 20% are common. The colorimetric method (14) was useless because of the excessive amounts of iron present in our samples. Complexing with thioglycolic acid in this method is only possible in samples containing not more than 100 μgm. of iron. Similarly the separation of iron from aluminum by precipitation in the presence of thioglycolic acid as suggested by Hummel and Sandell (15) was found to be quite accurate for fairly large samples of aluminum, over 100 mgm., but gave large random errors when used for samples containing 1 to 30 mgm. of aluminum. The iron exchange method of Teicher and Gordon (30) was also found to be of no value for these small amounts of aluminum. Therefore our interest was directed toward this potentiometric method which promised both accuracy and speed.

APPARATUS

The apparatus required is that normally used for potentiometric work—a sensitive potentiometer connected with two electrodes, in this case a calomel reference electrode and a bright platinum indicating electrode. The electrodes are inserted into a 30-ml. titration vessel which is fitted with a five-port cover. Four of the ports in the cover are located around the rim while the fifth is in the center. Titration from a 25-ml. standard burette or a 5-ml. microburette is carried out through the center port while air is excluded from the vessel by the introduction of a rapid stream of an inactive gas, carbon dioxide or nitrogen, playing on the surface of the solution through a fourth port. The burettes are to be accurate within the limits set by the United States Bureau of Standards for 'A' class volumetric glassware. The fifth port is reserved for the introduction of chemicals as required and is normally kept closed during titration so that the inactive gas escapes from the vessel around the tip of the burette. Stirring during titration is accomplished by means of a magnetic stirrer using a small, glass-covered rod $\frac{1}{2}$ in. long and 1/16 in. in diameter. The potentiometer used in our laboratory is the "Polymetron Model 42 Precision pH Meter" which is accurate to 0.01 pH or one millivolt when used as a potentiometer.

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PROCEDURE

The samples of pulp or paper are incinerated according to standard methods (29). The ash sample is then transferred to a weighed platinum crucible and weighed. It is wetted with distilled water to prevent spattering, and dissolved in 10 ml. of warm 1: 1 HCl. The acid solution and washings from the platinum crucible are filtered through a No. 42 Whatman paper into a 100-ml. volumetric flask, the filter paper being washed with three or four small portions of warm 1: 1 HCl, followed by distilled water until the flask is almost filled to the mark. When cool the flask is filled to the mark with distilled water and 20 ml. aliquots for the aluminum determination transferred to small beakers. These are evaporated to dryness under an infrared lamp to remove excess hydrochloric acid. The residue is redissolved in a few drops of 1: 1 HCl and 2 ml. of distilled water. When re-solution is complete this sample is washed with 8 ml. of saturated NaCl solution into the titration vessel. Absolute ethyl alcohol, 10 ml., is then added to the titration vessel. This causes some precipitation of the salt which provides a reservoir of ions so that the total ion activity during the titration remains practically constant. The cover of the titration vessel is then clamped into position and the magnetic stirrer started. The glass and calomel electrodes of the precision pH meter are then inserted through two of the ports in the cover and the pH of the solution is carefully adjusted to about 3.5 using 1/10 *N* solutions of sodium hydroxide and hydrochloric acid as required (see Table II).

The glass electrode is removed from the system after being washed with saturated salt solution. The neutral gas stream is started and the burette placed in position for titration. The solution of a ferrous salt required to complete the half cell with the ferric ions already present is added to the sample in the form of two drops of a 20% solution of ferrous chloride. It is desirable to make up fresh 10-ml. lots of this solution every four hours on days that the titration is used because it oxidizes very rapidly in the presence of air. This is also the reason why air is excluded from the titration vessel. At this point the platinum indicating electrode is inserted into the titration vessel and the pH meter is converted to read in millivolts. When the system reaches equilibrium, as indicated by a steady potential reading, titration may proceed using a standard sodium fluoride solution of appropriate strength: $\frac{1}{5}$ *N* when the aliquot contains more than 20 mgm. of aluminum, 1/10 *N* for more dilute samples.

If the approximate aluminum content is known, the titration may begin with fairly large portions, say 1 ml., of sodium fluoride, the potential reading being noted after each addition. Between each addition care must be taken to ensure that equilibrium is reached; the formation of the aluminum–fluoride complexes is a slow reaction and as long as five minutes between each addition of titrant may be required. The use of automatic titrating apparatus may reduce the time required for titration; this technique has not been attempted in this laboratory. On approaching the end point, which is indicated by a very rapid change in potential, no more than 1/10 ml. of titrant should be added

at a time. The end point is taken to be the point of maximum rate of change of potential. This does not coincide precisely with the equivalence point but the error introduced by this aberration is too small to be of practical importance.

THE TITRATION CURVE

Fig. 1 is an example of the type of titration curve obtained by this method. When about one-third to one-half of the titrant has been added to the ash solution there is a small abrupt decrease in potential which always occurs to a greater or lesser extent during this titration. Teodorovich (31) attributes this to the semiquantitative formation of the AlF_2Cl complex. This small inflection

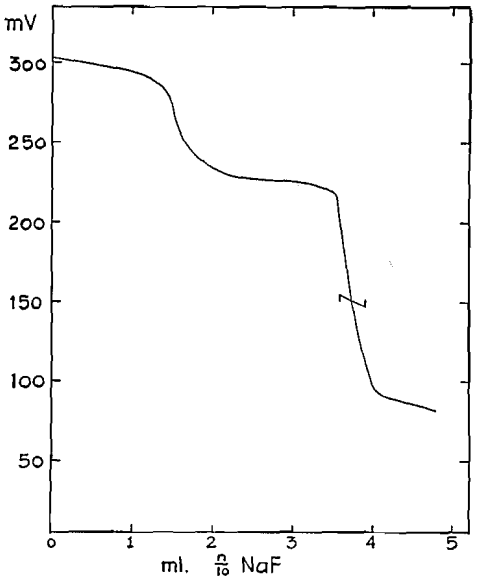

FIG. 1. A typical titration for aluminum in ash.

can be used as an indication of the approximate amount of sodium fluoride required in the titration and so the time taken per titration can be reduced. The time required for a titration is about 20 min.; the whole analysis for aluminum in pulp or paper ash can be done in about four hours, excluding the time required for ashing the paper.

INTERFERENCE

As calcium, magnesium, and beryllium can be determined by using this same potentiometric technique, some interference by them might be expected. However, it has been found in this laboratory and by other workers (17, 22) that the end point for aluminum is reached before complexing of the divalent cations with fluorine begins. If there are very large amounts of calcium and magnesium present in comparison to aluminum, the time taken for equilibrium to be reached after each addition of sodium fluoride is increased but there is no change in the final shape of the curve from the beginning of the titration to

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the equivalence point. The tail of the curve after the equivalence point has been passed does depend on the amount of calcium and magnesium present and also on the amount of ferric iron in the sample. The curve tends to flatten out in the presence of calcium and magnesium, as shown in Fig. 1, and to remain flat until the equivalence point for the magnesium is reached. This has been used as the basis of a titration for aluminum and magnesium in the absence of calcium. Excessive amounts of ferric iron (more than three times the amount of aluminum present) decrease the potential change of the aluminum equivalence point and make the analysis unreliable (16, 23).

ACCURACY OF RESULTS

The results in Table I present some analyses of artificial ash mixtures containing known amounts of aluminum and iron. The sodium fluoride used for

TABLE I

TITRATION OF ARTIFICIAL ASH MIXTURES CONTAINING KNOWN AMOUNTS OF IRON AND ALUMINUM

Sample	Total aluminum present, mgm.	Total Fe^{+++} present, mgm.	Total aluminum found, mgm.	Error, %
1	0.085	1.037	0.084	−1.2
2	0.085	3.111	0.083	−2.4
3	0.085	5.185	0.081	−4.9
4	0.212	2.074	0.212	0
5	0.212	5.185	0.213	+0.5
6	1.571	0.620	1.571	0
7	1.571	1.861	1.571	0
8	2.510	1.861	2.514	+0.2
9	10.600	7.314	10.604	+0.05

these titrations was standardized against known solutions of both aluminum chloride and aluminum sulphate. In both cases it was found that 1 ml. of sodium fluoride was equivalent to 0.220 mgm. of aluminum for titrations 1 to 5, and 0.419 mgm. for the remainder. This table shows that for titrations involving less than one milligram of aluminum, quite high accuracy is possible in the presence of up to four times as much iron as aluminum; more iron than this introduces large errors because the rate of change of potential at the equivalence point becomes less as the amount of iron is increased and it is difficult, with the present equipment, to judge where the maximum rate of change occurs. With such small samples titration must be carried out with great care using a microburette.

The results in Table II show what happens when the pH during titration is varied. The results at 3.00 pH are a little high, those at 3.25 and 3.50 are quite acceptable. At 3.75 pH the potentiometer pointer was drifting quite erratically near the end point which made the readings very unreliable. At pH 4 there was no change in the potential reading even after the addition of 6 ml. of sodium fluoride, 3.88 ml. being the required amount. Hence titration at a pH between 3.25 and 3.50 is required.

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TABLE II

Sample	Aluminum present, mgm.	pH at beginning of titration	Aluminum found, mgm.
1	1.624	3.00	1.661
2	1.624	3.25	1.623
3	1.762	3.50	1.762
4	1.624	3.75	1.561
5	1.624	4.00	0.000

SUMMARY

This method presents for the first time a technique whereby semimicro quantities of aluminum may be determined in the presence of relatively large amounts of iron with both accuracy and speed. The necessity for the separation of iron with its consequent risks of inaccuracy is eliminated. This renders the method suitable for routine analysis of very small samples. All previous applications of the potentiometric method to aluminum analysis have been on the macro scale.

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ANALYSIS FOR SMALL AMOUNTS OF CALCIUM, MAGNESIUM, BARIUM, AND SULPHATE USING PHTHALEIN PURPLE[1]

By J. R. McCallum[2]

ABSTRACT

For the determination of sulphate ion in samples containing 3 to 20 mgm., it was found that the standard precipitation techniques did not give sufficiently accurate results, and were time consuming. Reference to the literature showed that with certain modifications a complexometric method proposed by Schwarzenbach *et al.* for samples containing 20 to 50 mgm. of sulphate was most likely to give accurate results rapidly. In this method the sample is passed through a cation exchange column and washed with distilled water into a flask. This solution is boiled and precipitated with excess standard disodium ethylenediaminetetracetate in the presence of alcohol and ammonia using phthalein purple indicator. Provided that the details of procedure described in this paper are closely adhered to, accuracy is usually within two per cent. Calcium, magnesium, and barium may also be titrated directly using the phthalein purple indicator.

INTRODUCTION

During certain studies it became necessary to measure the amounts of sulphate present in samples of pulp and paper ash. It was required that the method chosen should measure quantities of sulphate weighing between 3 and 20 mgm. with an accuracy of three per cent or better. It should take no longer to perform than the standard gravimetric methods for larger samples.

Recourse to the literature produced references to several possible titrimetric methods. For example, Belcher and co-workers (2) precipitated and filtered as barium sulphate. This precipitate was then dissolved in excess standard ethylenediaminetetracetate and the solution back-titrated with a standard magnesium chloride solution to an eriochrome black (solochrome black) end point. Their results on samples containing 1 to 60 mgm. of sulphate are well within the limits mentioned above, but the method is tedious.

Munger and co-workers (3) precipitated the sulphate in slightly acid solution with a known excess of barium chloride. The mixture was boiled for a few minutes, cooled, and filtered. The filtrate was titrated to an eriochrome black end point. Their results with samples containing less than 20 p.p.m. of sulphate were not within the required limits. Sijderius (5, 6) followed much the same method and obtained results about 20% too low. He found it necessary to age the precipitate overnight as in the gravimetric methods and to filter before titration. Both Munger and Sijderius were troubled by the presence of carbonate and had to boil the original sample in a strongly acid medium before proceeding with the determination.

The main difficulty in these methods lies in the uncertainty of the eriochrome black end point. Munger (3) had to add a known amount of magnesium in order to make it sharp and clear. For this reason we became interested in a new indicator proposed in 1954 by Anderegg, Flaschka, Sallmann, and Schwar-

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Contribution from the Quebec North Shore Paper Company, Baie Comeau Mill, Baie Comeau, Que.
[2]*Research chemist, Quebec North Shore Paper Company.*

zenbach (1, 4). These publications suggested that a particular complex organic acid indicator could be employed in a relatively simple procedure to determine the alkaline earth metals and that it might be similarly useful for the titration of sulphate in samples containing 20 to 50 mgm. of the ion. The present paper indicates specific conditions under which it may be so employed to determine sulphate when present in an aliquot at 3 to 20 mgm.

PROCEDURE

The method as described in this paper was developed specifically for the analysis of pulp and paper ash, but there is no reason to believe that it could not be applied to problems of a more general nature.

The sample of pulp or paper is ashed according to standard procedures (7). The ash so obtained is transferred to a platinum crucible or dish and weighed. It is wetted with a little distilled water and dissolved in 10 ml. of warm 1:1 hydrochloric acid. The acid solution and washings from the platinum crucible are filtered through a No. 42 Whatman paper into a 100-ml. volumetric flask, the filter paper being washed with three or four small portions of warm 1:1 hydrochloric acid, followed by distilled water until the flask is almost filled to the mark. When cool, the flask is filled to the mark with distilled water and 20 ml. aliquots for the sulphate determination are transferred to small beakers. These samples are evaporated to dryness under the infrared lamp to remove excess hydrochloric acid. The residues are redissolved in two or three drops of warm 1:1 hydrochloric acid and diluted with about 5 ml. of distilled water. These samples are then transferred to the reservoir of an ion exchange column together with the rinsings from the beaker.

The ion exchange column used was Amberlite IR-120(H) in a column 2 cm. in diameter and 25 cm. long. It was found that such a column could be used for 10 samples before regeneration with 3 *N* hydrochloric acid became necessary.

The sample is passed through the column at a rate of 5 ml. per min. and collected in a 250 ml. flask, followed by three 50 ml. portions of distilled water. The final volume of the sample should not be much more than 175 ml.

This solution is heated to boiling and treated with an excess of standard 0.05 *N* barium chloride solution, added from a calibrated microburette. The mixture is then boiled down to about 50 ml. Porous pot may be used at this stage to reduce bumping. The sample is then corked and aged for at least an hour, preferably two hours, at 60° C. or higher, after which it is allowed to cool to room temperature (cf. Table II).

The cool sample is made neutral to methyl red with sodium hydroxide solution; then an equal volume of ethyl alcohol is added to it. Absolute alcohol or any grade which is free of sulphate and alkaline earths may be used. From this point the solution absorbs carbon dioxide readily and the remainder of the analysis should be carried out with dispatch. Concentrated ammonia solution, 5 ml., and five to seven drops of the indicator mixture to be described later are added to the solution. Back titration with standard 0.05 *N* ethylenediaminetetracetate solution is begun immediately from a calibrated microburette and continued drop by drop until the sharp change from deep blue

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through blue-green to yellow-green is complete. Almost invariably the color shifts back toward blue after the end point is reached for the first time; titration must be continued until a permanent yellow-green is established. This shift in color at end point becomes less and less noticeable as the aging time is increased. With overnight aging it is eliminated and it is suggested that, if convenient, the precipitate be aged overnight.

The above differs from the method of Schwarzenbach (4) in the concentration of several of the reagents, in the introduction of an aging period (which we have found essential to good results), and in the use of a microburette.

INDICATOR

The indicator for this titration was a mixture of 0.1 gm. phthalein purple,* 0.005 gm. methyl red, and 0.05 gm. dianil green† in 100 ml. of solution.

Schwarzenbach in his textbook (4) recommends the use of the phthalein purple by itself; the original paper (1) suggested a dye mixture similar to the above. We have tried both methods and recommend the use of the mixed indicator rather than phthalein purple alone because the mixture gives a much clearer end point. The shelf life of either indicator solution is about one week.

DETERMINATION OF THE ALKALINE EARTHS

For the titration of the alkaline earth metals the procedure is simple and direct, and our results confirm the recommendations of Schwarzenbach (4). The slightly acid solution, which must be free of ammonium salts, is adjusted to neutrality with sodium hydroxide (methyl red indicator) and made alkaline with 5 ml. of concentrated ammonia per 100 ml. of solution. Five to seven drops of phthalein purple or the mixed indicator are added to the sample giving a bright purple color. This mixture is titrated with a standard ethylenediaminetetracetate solution of strength appropriate to the sample being examined. The end point is a sharp change from the bright purple to a very pale pink or colorless condition. This requires but one drop of a 0.1 *N* ethylenediaminetetracetate solution. This method has been used by us to determine total water hardness and calcium, magnesium, and barium separately. The color change for magnesium is less sharp than for the others.

RESULTS

Table I gives the results for some analyses for sulphate on artificial ash mixtures. The "wash water" column indicates the amount used in the ion exchange step of the determination; the best results were obtained with 150 ml. wash. The last three samples also contained a little iron and silica; the exact quantities were not measured and so are not included in the table. It must be pointed out that to get results to agree as well as this it is necessary to follow all the details of the method as described above.

Table II presents two sets of results showing the effect of insufficient aging on the amount of sulphate found. Sufficient accuracy can be obtained after

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†*No. 576 Allied Chemical & Dye Corporation.*

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TABLE I

TITRATIONS FOR SULPHATE

Titration number	Sample containing Al, mgm.	Ca, mgm.	Mg, mgm.	SO_4, mgm.	Wash water, cc.	SO_4 found, mgm.	Error, %
1[a]				7.16	125	7.17	−0.14
2			0.78	3.10	125	3.16	+1.94
3	0.95			5.20	125	5.05	−2.88
4	0.19	2.97	0.31	3.71	125	3.74	+0.81
5	0.29	4.45	0.45	5.57	75	5.23	−6.28
6	0.38	5.94	0.62	7.42	75	7.24	−2.43
7	0.12	2.97	0.79	7.33	75	7.06	−3.68
8	0.18	4.45	1.17	11.00	150	10.92	−0.73
9	0.24	5.94	1.56	14.66	150	14.74	+0.55
10	0.30	7.43	1.95	18.33	150	18.60	+1.47

[a] = *Ammonium sulphate solution.*

TABLE II

EFFECT OF DIFFERENT AGING TREATMENTS
150 cc. of wash water used during ion exchange step

Sample No.	Aging time	SO_4 present, mgm.	SO_4 found, mgm.	%
1	0	4.41	3.53	80
1	15 min.	4.41	4.02	91.3
1	30 min.	4.41	4.07	92.3
1	45 min.	4.41	4.37	99.2
1	1 hr.	4.41	4.39	99.5
1	18 hr.	4.41	4.39	99.5
2	20 min.	7.33	6.84	93.3
2	35 min.	7.33	7.08	96.6
2	50 min.	7.33	7.27	99.1
2	65 min.	7.33	7.34	100.1
2	12 hr.	7.33	7.32	99.9

45 min. of aging but the end point is very broad at this time and it is only by very careful approach to it that the accuracy reported may be obtained. At one hour the accuracy is good though the end point is still a little obscure. An aging period of at least one hour, preferably more than two hours, is recommended.

Table III gives some results for the analysis of solutions containing calcium, magnesium, and barium. The second result was obtained on a sample originally containing both calcium and magnesium which were separated by precipitation of the calcium as oxalate in the presence of acetic acid. The other calcium samples were prepared by dissolving calcium carbonate in a little hydrochloric acid and diluting the solution to a standard volume. Aliquots were taken for the titrimetric analysis and these were checked by gravimetric analysis of larger aliquots by the usual method of precipitation as oxalate. Samples 4 and 5 were standard solutions of magnesium sulphate, and 6 and 7 of barium chloride.

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TABLE III

TITRATIONS OF CALCIUM, MAGNESIUM, AND BARIUM SOLUTIONS

Titration No.	Sample containing			Found		
	Ca, mgm.	Mg, mgm.	Ba, mgm.	Ca, mgm.	Mg, mgm.	Ba, mgm.
1	2.81			2.81		
2	3.21			3.24		
3	50.75			50.76		
4		0.41			0.41	
5		2.20			2.18	
6			3.49			3.50
7			7.00			6.98

ACKNOWLEDGMENT

Acknowledgment is made to the Ontario Paper Company, Ltd., for permission to publish this work.

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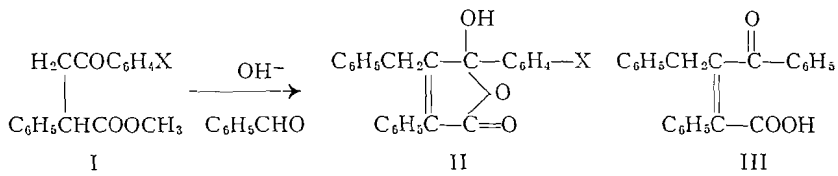
α-ARYL-β-AROYLPROPIONIC ACIDS AND THEIR CONDENSATION PRODUCTS WITH AROMATIC ALDEHYDES[1]

By C. F. H. Allen, T. J. Davis, D. W. Stewart, and J. A. VanAllan

ABSTRACT

It has been shown, by means of spectral analysis, that α-aryl-β-aroylpropionic acids exist in an open-chain configuration while the condensation products of these latter acids with aromatic aldehydes are lactols. The mesityl derivatives constitute exceptions in both series. These findings necessitate a revision of some of the earlier literature.

The investigation of the condensation products of γ-ketonic esters (I) and aromatic aldehydes showed certain inconsistencies between the para-substituted benzoyl series (X = Cl, Br, OCH_3) and the unsubstituted ketonic ester series (X = H) (2). It was postulated that the condensation products of benzaldehyde and methyl α-phenyl-β-benzoylpropionates gave lactols (II) when chloro-, bromo-, or methoxy-substituents were present in the para-position of the benzoyl group. In the case where X = H, it was concluded that, on the basis of the available experimental evidence,* the condensation product was the isomeric open-chain acid (III). The fact that substituents such



I II III

as methoxy and chloro, which have opposite electrical effects, produce a cyclized compound suggests that the unsubstituted compound should also be cyclic (II, X = H). The problem was therefore reopened with a view to resolving this discrepancy by means of ultraviolet and infrared absorption curves.

As a preliminary step, the ultraviolet and infrared spectra of several α-aryl-β-aroylpropionic acids, which serve as starting materials in the synthesis, were examined. The infrared spectra for these substances (Table I, with the exception of I*m*) all show a typical α,β-unsaturated carbonyl band at about 6.0 μ and an acid band at about 5.9 μ. The ultraviolet absorption spectra show a short-wavelength band in the region 242 mμ for I and I*j*; this is associated with the benzoyl absorption (cf. acetophenone, λ 245, ε = 10,000) (5) and is shifted slightly to longer wavelengths for those substances having an electron-donating

[1]*Manuscript received April 4, 1956.*
Contribution from the Kodak Research Laboratories, Rochester 4, New York. Issued as Communication No. 1787.

**In the original work on these lactols and aroylpropionic acids, their behavior, when they were treated quantitatively with an excess of methylmagnesium iodide, was used as a basis for determining structures. Although there were a few discrepancies, in view of the general agreement, it appeared reasonable to draw inferences from the experimental results. It is now obvious that the Grignard reaction is not a reliable tool for distinguishing between possible tautomeric structures.*

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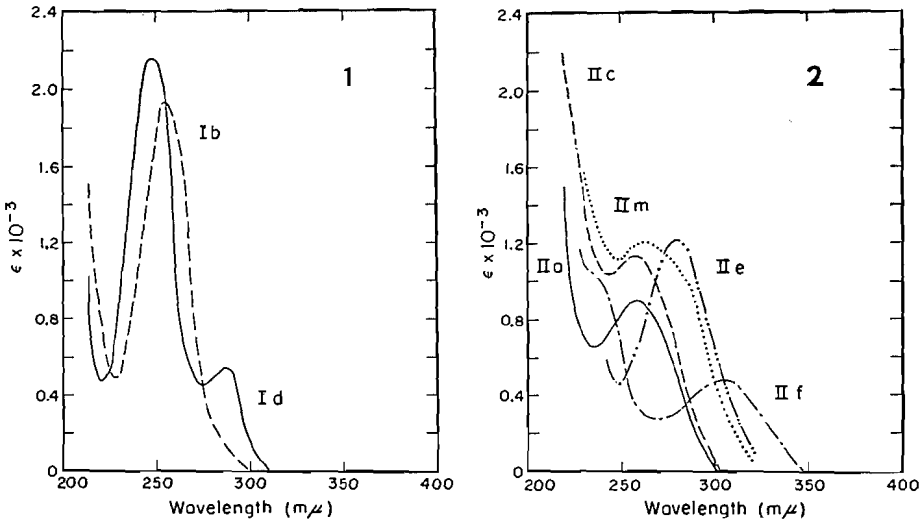
TABLE I

SPECTRAL DATA OF β-AROYLPROPIONIC ACIDS, $R_1CH(COOH)—CH_2COR_2$

				Infrared			Ultraviolet	
	R_1	R_2	m.p.,°C.	λ_{acid}	λ_{CO}	λ_{dimer}	λ_{max}	$\epsilon\times10^{-3}$
Ia	C_6H_5	4-FC_6H_4	161	5.90	5.98	3.8–3.9	255	19.5
Ib	C_6H_5	4-BrC_6H_4	160	5.87	5.93	3.6–3.9	255	19.5
I	C_6H_5	C_6H_5	150	5.9	5.97	3.7	242	14.6
Ic	C_6H_5	Mesityl	172	5.87	5.93	3.7		
Id	$CH_2O_2C_6H_4$	4-ClC_6H_4	189	5.9	5.97	3.7	248	21.0[a]
							287	5.5
Ie	H	Mesityl	109	5.86	5.93	3.7		
If	H	4-ClC_6H_4	130	5.9	5.95			
Ig	H	4-$CH_3C_6H_4$	129	5.9	5.95			
	Methyl esters							
Ih	$CH_2O_2C_6H_4$	4-ClC_6H_4	109				249	21.6
							288	5.4
Ij	$CH_2O_2C_6H_4$	C_6H_5	121				242	19.2
							286	5.5
Ik	C_6H_5	4-$CH_3C_6H_4$	112				252	18.0
Il	C_6H_5	C_6H_5	85–86	5.79	5.95			
Im	C_6H_5	Mesityl	60–61	5.82			258	0.57
							251	0.90
							263	0.52
In	C_6H_5	4-BrC_6H_4	120					

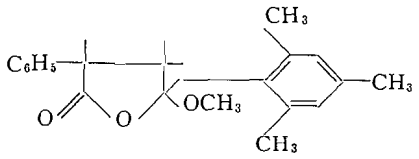
[a]*The spectrum of Id in 0.1 N NaOH has a* λ_{max} *at 255 mμ* ($\epsilon = 35.0\times10^{-3}$) *and a shoulder at 290 mμ.*

substituent in the benzoyl residues as in I*b*, I*d*, I*h*, and I*k*. The long-wavelength band in I*d*, I*h*, and I*j* arises from the independently absorbing methylenedioxyphenyl moiety (see Fig. 1). On the basis of the evidence just given, it is



FIGS. 1 AND 2.

clear that these substances exist with the open-chain configuration* in the solid state and in dilute solution. The one exception is methyl β-mesitoyl-α-phenylpropionate (I*m*), the spectrum of which shows clearly that it is the derivative of butyrolactone and has structure (IV).

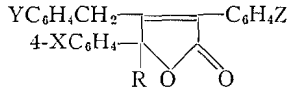


IV

The ultraviolet absorption spectra of lactols of the type II are collected in Table II. The maximum absorption of II*a*–II*n* occurs at about 260 mμ with a molar absorptivity of about 10,000.

TABLE II

SPECTRAL DATA OF SOME LACTOLS AND THEIR DERIVATIVES



						Infrared		Ultraviolet		Ultraviolet In alkaline soln.	
II	R	X	Y	Z	m.p.,°C.	CO	OH	λ_{max}	$\epsilon\times10^{-3}$	λ_{max}	$\epsilon\times10^{-3}$
a	OH	H	H	H	147	5.75	2.8	258	10.0	247	14.6
b	OH	Cl	H	H	134	5.75	2.8	260	10.5	257	16.9
c	OH	Br	H	H	157	5.85	3.1	259	11.4		
d	OH	CH_3O	H	H	122	5.85	3.1	267	10.2	280	16.0
e	OH	H	2-CH_3O	4-CH_3O	126	5.75	3.0	281	10.4		
f	OH	Cl	H	CH_2O_2	153	5.80	3.1	305	7.0		
g	OCH_3	H	H	H	119	5.75		260	10.5[a]		
h	OCH_3	Cl	H	H	82	5.75		260	11.1[a]		
j	OCH_3	Br	H	H	78	5.70		260	10.5		
k	AcO	H	H	H	128	5.65		260	10.0		
l	AcO	Cl	H	H	159	5.67		260	10.7[b]		
m	AcO	Cl	CH_2O_2	H	174	5.67		258	12.0		
n	Cl	C_6H_5	H	H	150	5.63		260	22.4		

[a]*Same in basic and acetic solutions.*
[b]*Ring opened by alkali.*

The unsaturated lactone (V) has been previously observed to have an absorption maximum at 257 mμ with an extinction coefficient of $\epsilon = 9820$ (4). This similarity in ultraviolet absorption of the lactols and the lactone (V),

**These acids (see Table I) show approximately one active hydrogen and two additions by Grignard analyses; the reagent, in butyl ether, was added to the substance in xylene. These results are at variance with those previously reported (which were done entirely in butyl ether) and with the anticipated results, i.e., one addition and one active hydrogen; the corresponding esters show three additions, as expected. Here again, the mesityl derivative, Ie, shows anomalous results, i.e., 0.0 addition and 3.2 active hydrogen. It must be concluded that the method of Grignard analysis is of little use as a diagnostic tool in this series.*

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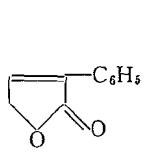
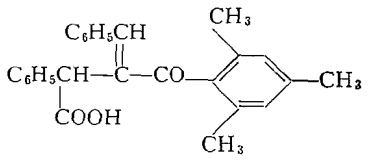


V

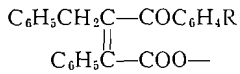


VI

together with the infrared spectra which show a band at 5.75 ± 0.10 μ, is characteristic of all members of the series and is associated with the carbonyl oxygen of the five-membered ring. Electron-donating substituents in the lactols in positions other than the Z-position (see Table II) do not affect the ultraviolet absorption. In contrast, alkoxy substituents in the Z-position, as in *e* and *f*, produce a bathochromic shift to 281 mμ and 305 mμ, respectively. This suggests that the ultraviolet absorption in this series of lactols is of the styrene type (see Fig. 2). The mesityl derivative (3), on the basis of its ultraviolet (λ_{max} 285 (ϵ = 16,300)) and infrared spectra (5.87 μ and 6.07 μ), is still regarded as the open-chain acid (VI). It shows one active hydrogen (COOH) and one addition (1,4-addition to α,β-unsaturated ketone linkage).

The addition of base to the spectral solution of *a* and *d* produces a small hypochromic shift in *a* and *b*, and a bathochromic shift in the spectrum of *d*; increased absorption was noted in all cases. The maxima for these three substances are presumably due to the benzoyl group functioning freely in the open-chain anionic form since acetophenone and its 4-chloro and 4-methoxy derivatives have maxima in approximately the same position (see Table I for the comparison).

The chalcone absorption which one might expect for this ionic substance (VII) is suppressed by reason of the nonplanarity of the molecule. Steric

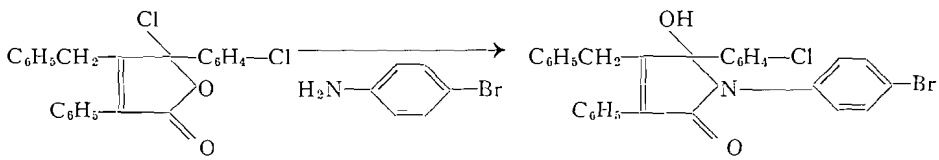


VII

considerations show that the planarity of such a system must be strongly hindered.

The addition of acid or bases to the spectral solutions of the methyl ethers *g* and *h* effected no essential change in either the magnitude or the wavelength of absorption, thus indicating a stable cyclic structure in the case of the methyl ether.

Finally, the structure of the reaction product obtained from the reaction of the cyclic chloride (VIII) with *p*-bromoaniline (1) has been revised to that



VIII IX

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of the lactamol (IX). The ultraviolet absorption spectrum has a $\lambda_{max} = 248$ ($\epsilon = 26{,}000$) and the infrared shows a strongly developed OH bond. Both of these properties are in agreement with the structure assigned.

In view of these findings, the structure of the compounds described (1, 2, 3) should be revised accordingly, i.e., all mesityl derivatives and compound II*g* and its derivatives, the chloride, acetate, and ester. The latter substances are now assigned a cyclic structure.

ACKNOWLEDGMENT

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REACTIONS OF ARYLSULPHONIC ESTERS

V. AN INTERPRETATION OF ACTIVATION ENERGIES OF SOLVOLYSIS OF METHYL BENZENESULPHONATE IN MIXED HYDROXYLIC SOLVENTS[1]

By J. B. Hyne[2] and R. E. Robertson

ABSTRACT

The rates of solvolysis of methyl benzenesulphonate at 50° and 75° C. in several binary aliphatic alcohol–water mixtures have been determined over the composition ranges. The derived activation energies are compared with those calculated from an extended form of the equation employed in accounting for solvolytic activation energies in pure hydroxylic solvents. The physical significance of the equation is discussed in terms of a spectrum of solvolytic mechanisms covering the range between S_N1 and S_N2 mechanisms. The equation predicts activation energy values well within the experimental uncertainty. Product ratio and activation entropy data are shown to be in keeping with the reaction mechanism proposed.

INTRODUCTION

In the previous paper of this series (8) we established a semiempirical equation relating the activation energies of solvolyses of benzenesulphonic esters in pure hydroxylic solvents. The success of this equation in predicting the activation energies of solvolyses in pure solvents prompted us to attempt to apply a similar treatment to the solvolyses of benzenesulphonic esters in mixed hydroxylic solvents. In this paper we have extended the original equation to enable the mixed solvent work to be treated and show that remarkably good prediction of the behavior of activation energy with solvent composition is possible.

Several other workers (2, 5, 6, 7) have recently made kinetic studies of solvolytic reactions in mixed solvents, notably Tommila and co-workers (16, 17, 18, 19, 20), but in most of these cases only one of the solvent species is solvolytically reactive. In the present work both hydroxylic solvents are reactive and the success of the treatment of activation energies employed is shown to be consistent with the intermediate mechanism (S_N12) postulated in the previous paper (8) for solvolyses in pure solvents.

EXPERIMENTAL

(a) *Preparation of Materials*

Methyl benzenesulphonate.—Eastman Kodak White Label further purified by fractional recrystallization from the melt to constant melting point, 4.50° C.

Water.—Distilled water passed through an ion exchange column (13).

Methanol.—Reagent grade material distilled from 50 gm. magnesium per liter at 64.6°–64.7° C. at 760 mm.

Ethanol.—Stock material distilled from 20 gm. of sodium and 30 ml. diethyl phthalate per liter at 78.4°–78.5° C. at 760 mm.

Isopropanol.—Stock material distilled from 50 gm. aluminum per liter under nitrogen flow through a 20 plate Stedman column at 82.2°–82.4° C. at 760 mm.

Tert-butanol.—Stock material purified by fractional recrystallization from the melt to constant m.p. 25.0° C. (three recrystallizations).

[1]*Manuscript received January 23, 1956.*
Contribution from the Division of Pure Chemistry, National Research Council, Ottawa, Canada. Issued as N.R.C. No. 3977. This paper was presented at the 129th Meeting of American Chemical Society, Division of Organic Chemistry, Dallas, Texas, April, 1956.
[2]*National Research Council of Canada Postdoctorate Fellow 1954–56.*

Benzenesulphonic acid.—Eastman Kodak (practical) used without further purification.

(*b*) *Preparation of Solutions*

Stocks of all solvent mixtures were prepared by weight. Approximately 0.1 gm./liter of benzenesulphonic acid was added to the stock solvent mixtures as a backing electrolyte. Working solutions were prepared in 100 ml. lots immediately prior to each run, 0.1 (±0.01) gm./liter of methyl benzenesulphonate being added from a previously calibrated capillary pipette.

(*c*) *Method*

The conductimetric method described by Robertson (13) was used down to 0.5 mole fraction of water. Conductance cells were not degassed in view of the risk of altering the composition of the solvent mixture. No complications arose from air bubbles on the electrodes. Owing to the known variation of degree of dissociation of benzenesulphonic acid with concentration in low dielectric solvent mixtures, several check determinations of rates were made in alcohol–water mixtures near the limit of alcohol concentrations studied. These checks were carried out by a continuous titrimetric method employing a differential colorimeter as end point indicator (14). This method is independent of degree of dissociation of the acid. The checks are shown in Table I. No check was made in methanol as any dependence of degree of dissociation on concentration in methanol–water mixtures would be less than in ethanol–water for which checks were obtained. Rate determinations at 0.738 mole fraction ethanol and 0.496 and 0.750 mole fraction isopropanol were not checked but previous investigations of the effect of dissociation on conductance rate determinations carried out in this laboratory indicate the values obtained are not in error to greater than ±1%.

TABLE I

COMPARISON OF CONDUCTIMETRIC AND TITRIMETRIC RATE DETERMINATIONS

Alcohol	Mole fraction alcohol	Conductimetric $k\times10^{-4}$ (sec.$^{-1}$)	Titrimetric (14) $k\times10^{-4}$ (sec.$^{-1}$)
EtOH	0.527	3.47[4] (±0.3%)	3.44[4] (±0.7%)
isoPrOH	0.261	3.98[5] (±0.1%)	3.98[4] (±0.8%)
tert-BuOH	0.182	3.84[5] (±0.3%)	3.85[7] (±0.3%)

All rate determinations in pure alcohols were by the normal titration method described by Robertson (12). Two rate determinations by this titrimetric method in ethanol–water mixtures previously reported by Robertson (12) are also included in Table II, and are in excellent agreement with the curve drawn through points determined conductimetrically.

(*d*) *Temperature Control and Time*

The same thermostatic control and temperature determination apparatus was employed as reported previously by Robertson (13). Temperature was controlled to ±0.003° C. and time measurement was accurate to better than 0.1 sec. per hr.

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(*e*) *Precision of Results*

The reproducibility of conductimetric rate determinations at both temperatures is recorded in Table II and except in those isopropanol–water mixtures previously mentioned was better than ±0.5%. This precision in k gives a precision of at least ±80 cal./gm-mol. in the activation energy calculated over the 25° C. range. Titrimetric rate determinations were not of the same precision, k's being found to better than ±1% and activation energies to ±150 cal./gm-mol. Although a precision of ±80 cal./gm-mol. is claimed for the activation energy the accuracy is unlikely to be of such a high order in view of the neglect of the ΔC_p of activation. The hydrolysis of methyl benzenesulphonate has a ΔC_p of activation of −31.6 cal./°C. and a somewhat lower value for alcoholysis (unpublished). In the absence of ΔC_p data for all water–alcohol mixtures used, however, a comparison of E_a's as calculated is all that is possible at present. A similar error would be present in all determinations, however, and from a comparative viewpoint the results do not lose significance.

TABLE II

SOLVOLYTIC RATE DATA FOR METHYL BENZENESULPHONATE IN WATER–ALCOHOL MIXTURES AT 50.0 AND 75.0° C.

Alcohol	Reference	Mole fraction alcohol	Vol. fraction alcohol	Dielectric constant of mixture D_{20}	$k \times 10^{-5}$ (sec.$^{-1}$)	± % k	t(° C.)	$k \times 10^{-4}$ (sec.$^{-1}$)	± % k	t(° C.)	E_a(obs.) (cal./gm-mol.)	E_a(calc.) (cal./gm-mol.)	ΔE_a	log PZ_{60}(obs.)
	(9)	0.000	0.000	80.4	19.66	0.4	50.003	19.34	0.2	74.906	20,520	20,470	+ 50	10.1811
Methanol		0.052	0.109	76.5	17.58	0.1	49.868	17.16	0.3	74.894	20,302	20,490	−188	9.976
		0.147	0.279	69.4	13.61	0.8	49.868	13.24	0.3	74.895	20,271	20,574	−303	9.844
		0.255	0.434	62.4	10.23	0.2	49.985	9.980	0.4	74.893	20,387	20,676	−289	9.798
		0.499	0.689	49.5	5.705	0.1	49.985	5.555	0.2	74.633	20,556	20,911	−355	9.658
	(12)	1.000	1.000	32.4	1.63		50.0	1.09		70.0	20,973	21,264	−291	9.317
Ethanol		0.026			17.66		49.888							
		0.071	0.199	70.8	13.95	0.5	49.910	13.40	0.3	74.901	20,249	20,376	−127	9.840
		0.111	0.288	66.1	10.93	0.1	49.881	10.64	0.3	74.892	20,277	20,354	− 77	9.753
		0.134	0.334	63.6	9.900	0.4	49.888	9.396	0.1	74.892	20,051	20,346	−295	9.557
		0.202						7.152	0.1	74.893				
		0.225	0.485	54.9	6.770	0.5	49.844	6.660	0.5	74.911	20,371	20,346	+ 25	9.608
	(12)	0.236			6.60		50.0							
		0.382			4.670	0.7	49.770							
		0.386	0.671	43.6	4.578	0.2	49.883	4.415	0.1	74.633	20,376	20,372	+ 4	9.442
		0.527	0.783	36.8	3.540	0.5	49.869	3.474	0.3	74.905	20,349	20,388	− 39	9.311
	(12)	0.552			3.34		50.0							
		0.738	0.901	30.1	2.330	0.1	49.887	2.298	0.2	74.887	20,394	20,383	+ 11	9.160
	(9)	1.000	1.000	25.0	rates at 70, 80, and 90° C.						20,400	20,354	+ 46	8.847
Isopropanol		0.025	0.097	74.7	16.81	0.1	49.867	15.81	0.4	74.893	19,970	20,350	−380	9.732
		0.060	0.212	67.7	11.40	0.1	49.886	10.90	0.3	74.900	20,118	20,225	−107	9.663
		0.126	0.379	56.5	6.490	0.2	49.867	6.453	0.3	74.895	20,466	20,089	+377	9.653
		0.264	0.604	40.4	4.141	0.4	49.869	3.985	0.1	74.891	20,175	19,960	+215	9.262
		0.496	0.807	26.0	2.631	0.5	49.886	2.422	0.1	74.900	19,779	19,836	− 57	8.795
		0.750	0.927	20.7	1.740	0.2	49.886	1.540	0.1	74.900	19,429	19,607	−178	8.381
		1.000	1.000	18.6	0.8191	0.1	49.886	0.6985	0.2	74.900	19,150	19,414	−264	7.870
tert-Butanol		0.025	0.117	72.2	14.94	0.2	49.978	14.25	0.2	74.894	20,185	20,250	− 65	9.825
		0.050	0.214	65.0	9.520	0.1	49.978	9.027	0.3	74.894	20,133	20,090	+ 43	9.595
		0.102	0.371	52.7	5.543	0.2	49.978	5.315	0.1	74.893	20,234	19,858	+376	9.429
		0.182	0.538	38.4	4.026	0.1	49.969	3.845	0.3	74.897	20,197	19,674	+523	9.265

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RESULTS

In Table II are collected the observed rates and percentage errors at each composition for the two temperatures employed. In all calculations the following values of standard constants were used: $T°$ A. $= 273.16+t°$ C.; $R = 1.987$; $\log_e 10 = 2.3026$. Solvent composition is given as both mole and volume fraction for later convenience as is the dielectric constant of the solvent mixtures (1). The Arrhenius activation energy derived from the observed rates, E_a(obs.), and the corresponding log PZ value at 50° C. are also recorded.

APPLICATION OF EQUATION TO MIXED SOLVOLYSIS OF METHYL BENZENESULPHONATE

The semiempirical equation of the previous paper (8)

$$[1] \qquad E_a = -47.18(D-\alpha+1.43(MV))+25{,}580$$

is not in suitable form to handle mixed solvolysis since the (MV), molecular volume, term is composite in this case. The (MV) term, however, can be expressed as a function of the volume fractions (ν) and molecular volumes (MV) of the two components of the solvent mixture and the extended equation

$$[2] \quad E_a = -47.18(D-\alpha+1.43(\nu_{H_2O}(MV)_{H_2O}+\nu_{alcohol}(MV)_{alcohol}))+25{,}580$$

can be applied in the mixed solvolyses cases. D is the dielectric constant of the solvent mixture at 20° C. and α is a constant characteristic of the ester. The α values for various benzenesulphonic esters were established in the previous paper (8) based on an arbitrary value for methyl benzenesulphonate of $\alpha = 0$. The E_a(calc.) values for the solvent compositions studied were calculated from equation [2] and are compared in Table II with the E_a(obs.) values obtained directly from the observed rates. Fig. 1 compares the observed and calculated values plotted for each solvent mixture across the composition range. The most striking feature of the comparison is the prediction by the extended equation of the reversal of dependence of activation energy on solvent composition on varying the alcohol component through the series methanol, ethanol, isopropanol, *tert*-butanol. In all but a few instances the agreement between E_a(obs.) and E_a(calc.) is good to 300 cal. In Figs. 1(*b*) and 1(*c*), an alternative dotted line is drawn through the experimental points at the aqueous end of the solvent composition range. This arises from doubt as to the accuracy of the determined E_a at approx. 0.13 mole fraction alcohol. The individual rate determinations leading to these values were quite reproducible but the abnormal behavior of the log PZ function in Fig. 4 at these same solvent compositions suggests that they may be in error. This source of doubt, however, does not affect the validity of the general trend observed.

To test the validity of the extended equation in cases where α was not zero, two previous results of Robertson (12) for the activation energy of mixed solvolysis in 50/50 v/v ethanol–water of isopropyl benzenesulphonate ($\alpha = 42$) and isopropyl *p*-methyl benzenesulphonate ($\alpha = 55$) were compared with the calculated values. The comparison is shown in Table III.

The agreement is well within the experimental error of the E_a's showing the validity of equation [2] when α is not zero.

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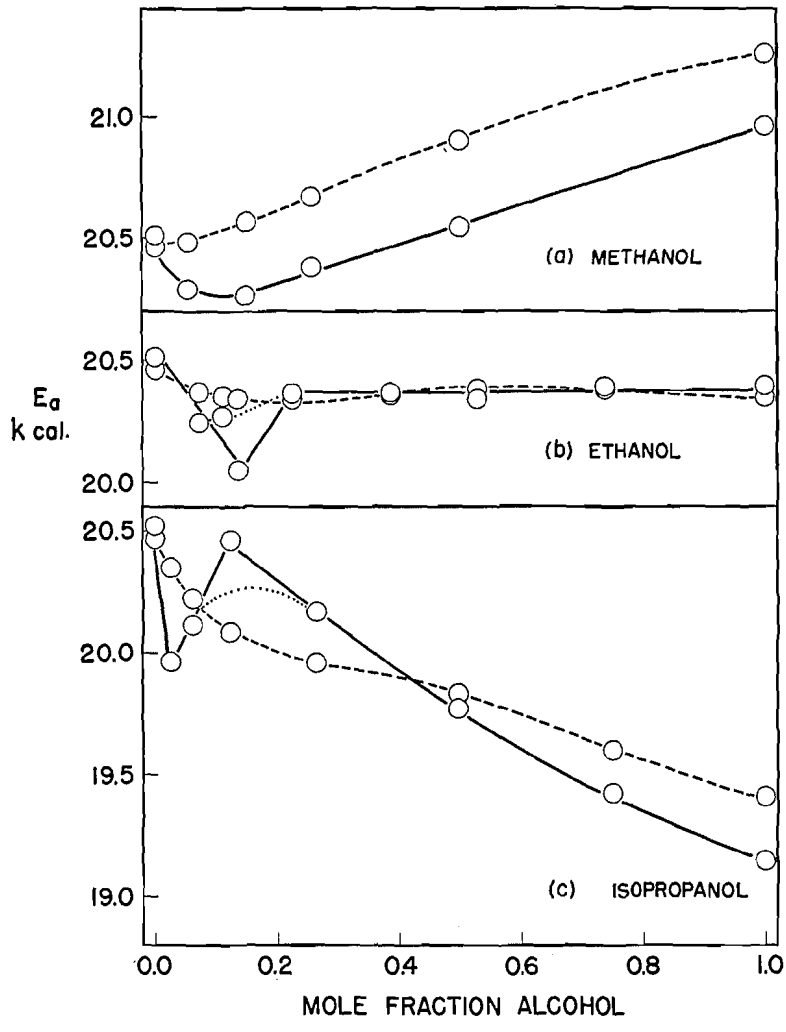

FIG. 1. ——— Observed. - - - - Calculated.

TABLE III

Ester	α*	Mole fraction ethanol	Vol. fraction ethanol	Dielectric constant mixture D_{20}	E_a(obs.) (cal./gm-mol.)	E_a(calc.) (cal./gm-mol.)	ΔE_a
isoPr-*p*H	42	0.236	0.500	54	22,259	22,370	−111
isoPr-*p*Me	55	0.236	0.500	54	22,843	22,997	−154

*α *values from previous paper this series (8).*

DISCUSSION

(a) *Proposed Mechanism of Mixed Solvolysis*

The S_N12 spectrum of mechanisms proposed in the previous paper (8) and envisaged as operative in all solvolytic reactions intermediate in mechanistic character between the limiting S_N2 and S_N1 types is based upon the principle

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that charge separation in the breaking bond of the ester precedes the onset of covalent interaction between the ester molecule and the solvent species. When covalent interaction and charge separation take place at the same point on the reaction parameter the mechanism is of the accepted S_N2 type (the one-stage process); as covalent interaction enters progressively later in the reaction relative to the charge separation, there is a tendency to formation of solvation stabilized intermediate ester species. These intermediates are characterized by a specific degree of charge separation in the breaking bond and the stability of the intermediate arising from solvation will be greater for greater charge separation. In the limit, as covalent interaction enters very late in the reaction process, charge separation proceeds to completion and a solvation stabilized ionic intermediate is formed characteristic of the pure S_N1 mechanistic type. It is, therefore, proposed that there is a *gradual* transition in mechanistic type from S_N2 to S_N1 so that each solvolytic reaction having intermediate character can be placed in its relative position on the mechanistic spectrum. It is impossible on the evidence presently available to do more than guess at what point in the spectrum an actual intermediate appears. Doering and Zeiss (4) appear to favor the idea that an intermediate of very low stability is formed immediately the reaction characteristics depart from pure S_N2 behavior. This may be the case but the possibility remains that some intermediate S_N12 mechanisms having marked S_N2 character may be operative in which no true stabilized intermediate exists. The location of the range occupied by the solvolytic mechanisms of the benzenesulphonic esters on the S_N12 mechanistic spectrum cannot, therefore, be established conclusively. For simplicity of presentation, however, we have assumed that the most "S_N2-like" of these solvolytic mechanisms, viz. that of solvolysis of methyl benzenesulphonate, is characterized by the formation of a solvation stabilized intermediate. In Fig. 2 are shown the proposed stages in the mechanism of mixed solvolysis of methyl benzenesulphonate. The solvent stabilized intermediate ester species, involving

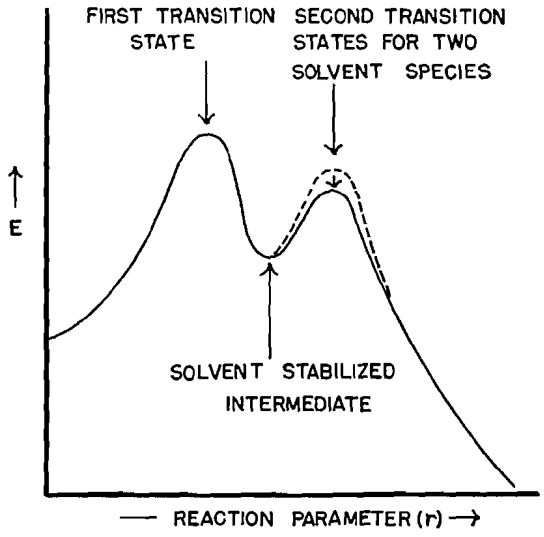
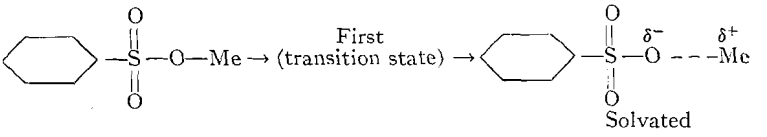


FIG. 2.

charge separation in the ester bond eventually to be broken, is reached through a rate-determining transition state with very little if any covalent interaction between ester and solvent molecules. This transition state, and subsequent intermediate, are then common to both the hydrolysis and alcoholysis in the case of mixed solvolysis and this being the rate-determining stage the observed activation energy is associated with this single process.



In the case of solvolysis in pure solvents the detailed nature of solvation of the intermediate was not defined (8) since all solvating species were identical. In mixed solvolysis, however, we have two hydroxylic solvent species participating in the solvation of the intermediate. There will be competitive solvation by both components of the solvent mixture, the extent to which each species will be involved in the primary solvation shell depending upon the relative activity of the two species in the solvent mixture. The positions of the species in the solvation shell must be energetically equivalent. This is a necessary condition for a common solvent stabilized intermediate for both subsequent reactions. On passing to the second transition state one of the solvating species must attain a preferred covalent reaction position relative to the charge separated ester bond. The species adopting this position, either water or alcohol, will be determined by the relative abundance of the two species in the solvation shell which in turn is dependent upon the relative activities of the two species in the solvent mixture. The ratio of the products of the hydrolysis and alcoholysis should then be dependent upon the activity of the respective solvents

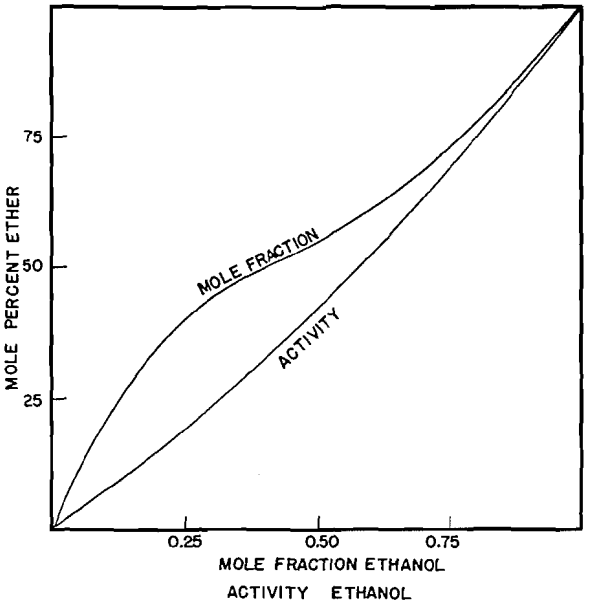


FIG. 3.

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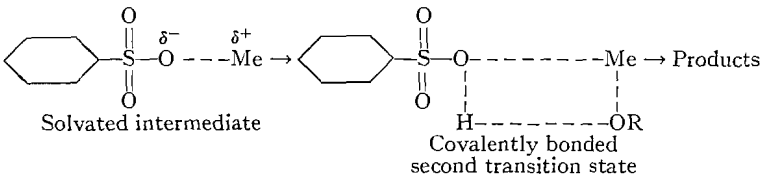
in the mixture. In Fig. 3 the mole per cent of ether (product of alcoholysis) is plotted against both mole fraction and activity of ethanol in the solvent mixture. The dependence of the ether product percentage on activity of the alcohol shows only slight negative deviation from linearity. The details of this product ratio work will be published shortly (10). Covalent interaction between one of the solvation shell molecules and the ester in the second transition state will be characterized by a specific activation energy for each reacting solvent species. Two possible transition states therefore exist in the second stage but of lower energy than the first common transition state so that they are not involved in the rate-determining process as shown in Fig. 2.



(*b*) *Failure of Equation in Highly Aqueous Solvent Mixtures*

Inspection of Fig. 1 shows that equation [2] fails to predict the marked minimum in E_a(obs.) noted in highly aqueous compositions. Similar behavior was noted by Tommila (16) in recent work on the solvolysis of benzenesulphonic esters in acetone–water and dioxane–water mixtures. Tommila offers a preferential solvation explanation for this behavior stating that the minimum indicates high solvation and high polarity of the initial state. We would suggest that the minimum observed in the work presented here is indicative of preferential solvation by the alcohol component. In such circumstances the microdielectric about the ester molecule would be markedly reduced below that expressed by the bulk dielectric (D_{20}) for the mixture and charge separation would consequently be less, favoring a more "S_N2-like" mechanism with a lower over-all activation energy. Furthermore it is seen from Fig. 3 that the plot of product ratio against mole fraction of alcohol shows an excess of the alcoholysis product (ether) at high water compositions in keeping with the suggestion that there is preferential alcoholic solvation. Attention is also drawn to the work of Martin and Brown (11) and others (3, 15) who have shown by various studies that at high aqueous concentrations in alcohol–water mixtures the water molecules tend to form water–water bonds preferentially within the solvent lattice. Greater energy would then be required to remove water molecules from the lattice for a solvation role than to remove alcohol molecules. Once a sufficiently high alcohol concentration has been reached to break up the quasi-crystalline water lattice the water will be more readily available for solvation. It is, therefore, not surprising that the simple relationship used to describe the solvent participation, viz. the molecular volume expression, does not reflect this special property of the system.

An attempt has been made to apply equation [2] to solvolysis in water–acetone and water–dioxane mixtures. The equation fails to predict the behavior of the activation energy over the composition range. This could be the result

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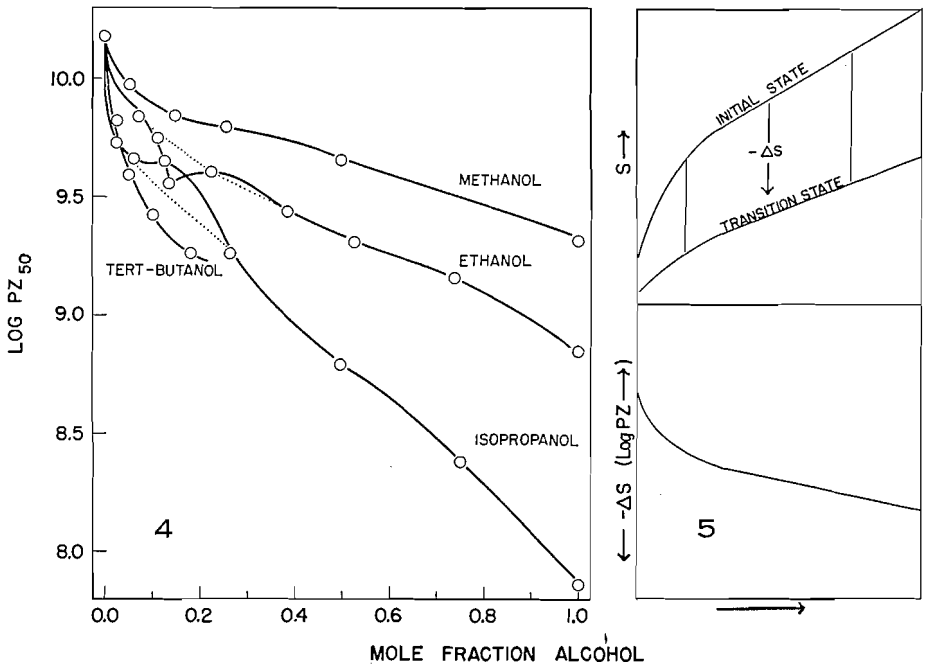
of simplifying assumptions made in establishing the original equation in the previous paper of this series (8). Here it was assumed that all solvent–solvent hydrogen bonds were of the same O–H - - - - O energetic type. This may be an acceptable approximation in mixtures of hydroxylic solvents but with the carbonyl and ether oxygen groups of acetone and dioxane the validity is questionable.

(*c*) *Discussion of Mixed Solvolytic Activation Entropies*

In discussing the variation of entropy of activation (ΔS) in terms of the log PZ function for the solvolysis of a given ester in a series of pure solvents (see Part IV this series (8)) we suggested that the increase in the negative ΔS value was due to a more rapid increase in the entropy of the initial state compared with the increase in entropy of the transition state as we proceeded along the solvent series. As expected the negative ΔS value also increases in passing through the composition range of mixtures of two solvents in the series. Generally speaking the increase in $-\Delta S$ (decrease in log PZ) bears a roughly linear relationship to the mole fraction of the alcohol (Fig. 4). There are some interesting deviations, however, which can be explained on the basis of the principles employed in discussing the behavior of the activation energies.



FIGS. 4 AND 5.

In all four mixed solvent cases studied here there is an initial drop in log PZ (increase in $-\Delta S$) tending to level off as the mole fraction of alcohol increases and then proceeding more or less linearly to the pure alcohol. Let us consider

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only the case of the methanol–water mixtures since the other cases behave similarly. We have, from previously discussed evidence, suggested that there is preferential solvation by the alcohol component in highly aqueous mixtures. How will such preferential solvation affect the activation entropy? In both the initial and transition states preferential solvation by alcohol over water would result in higher entropy because of the reduction in degree of ordering possible about the ester molecule in the case of the bulkier alcohol molecule. In the initial state this increase will be more marked than in the transition state owing to the weaker orientation forces of the dipolar ester molecule. Although the same steric argument applies in orientation about the transition state the stronger orientating forces arising from the partial charges will reduce the effect and the entropy will increase more slowly as a function of composition. In Fig. 5 the suggested behavior of the entropies of the initial and transition states is shown and the consequent behavior of the difference in entropy ($-\Delta S$) plotted. As is seen an initial increase in $-\Delta S$ (decrease in log PZ) is predicted followed by a linear trend to pure alcohol in a manner similar to the observed data plotted in Fig. 4.

Without introducing any further modifications of the model upon which the activation energy behavior was explained we can interpret the general behavior of the activation entropies and by refining the picture of solvent–solvent interaction in mixed solvents we can qualitatively account for minor deviations from this general behavior.

CONCLUSIONS

By extension of the semiempirical equation used in the previous paper of this series to correlate the activation energies of solvolyses of benzenesulphonic esters in pure solvents we have shown that solvolytic activation energies in mixed hydroxylic solvents may be treated in a similar manner. While the extended equation accounts for the gross behavior of the activation energies as a function of solvent composition further refinements are required in the molecular model used to account for minor deviations not predicted by the equation. These modifications are shown to be in keeping with the conclusions of other workers and are satisfactorily applied in a suggested treatment of the activation entropies. The work presented in this paper serves as a further test of the validity of the basic assumptions made in the previous paper in establishing the form of the semiempirical equation for solvolytic activation energies.

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A METHOD OF RECORDING a-c. POLAROGRAMS ON A CONVENTIONAL d-c. POLAROGRAPH[1]

By D. M. Miller[2]

ABSTRACT

An increase in the usefulness of the recording polarograph is obtained by a modification which allows either a-c. or d-c. polarograms to be obtained from it. A description of such a modification performed on the Sargent Model XXI is given in detail. A comparison of a-c. and d-c. polarography is made and illustrated by polarograms obtained from this instrument.

INTRODUCTION

Polarography with alternating currents has been investigated by a number of authors but the most extensive work is that of Breyer *et al.* (*vide infra*). Basically the method consists of impressing a small sinusoidal alternating voltage of low frequency on the direct potential applied to a dropping mercury electrode. This results in an applied e.m.f. which varies between limits determined by the amplitude of the a-c. voltage (ΔE, Fig. 1). Should the current

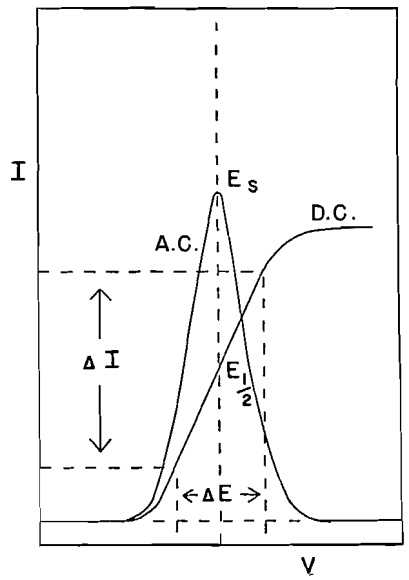

FIG. 1. Comparison of a-c. and d-c. polarograms.

be higher at the upper limit than at the lower limit of this voltage variation (as on the rising portion of the d-c. polarogram) an alternating current ΔI would be produced. This alternating current is measured as a function of the impressed direct voltage resulting in a plot which is essentially the derivative

[1]*Manuscript received April 4, 1956.*
Contribution No. 72, Science Service Laboratory, Canada Department of Agriculture, University Sub Post Office, London, Ontario, Canada.
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of the normal d-c. polarogram. Thus the waves produced in conventional polarography are replaced by a series of peaks, the summit potential (E_s) of which corresponds to the half wave potential ($E_{\frac{1}{2}}$) of the depolarizer (4).

A characteristic of this method is that only reversible electrode reactions give an a-c. peak. Breyer, Bauer, and Hacobian (3) have discussed the conditions which lead to reversible and irreversible electrode processes. They point out that reversible electrode reactions may be either polarographically reversible or irreversible depending on relative rates of the diffusive and electrochemical processes, and whether or not secondary reactions occur. Irreversible electrode reactions do not give a-c. polarograms. The reduction of oxygen therefore does not interfere directly in a-c. polarography and in general need not be removed.

Under the proper conditions the height of the a-c. wave produced by inorganic ions is directly proportional to the concentration of the ion (5). Best results are obtained in the range 10^{-4} M to 10^{-3} M with a limit of sensitivity of 10^{-5} M.

Since at the completion of the a-c. wave the current has returned to that of the ground solution, waves at more negative potentials are not affected by those of nobler ions. This means that small amounts of one ion may be determined in the presence of large amounts of ions reduced at more positive potentials, a difficult or impossible procedure with d-c. polarography.

Owing to the higher current obtained with the a-c. polarograph the effect of circuit resistance is much more pronounced. Breyer, Gutman, and Hacobian (6) have used mercury pool electrodes to reduce cell resistance but the author has found the usual H-cell to have an equally low resistance plus the advantage of a reference electrode.

The a-c. polarography of a number of ions has been studied by Breyer, Gutman, and Hacobian (5, 6, 8, 9). Cations were found to produce normal waves while the anions studied (9) produced very sharp anodic waves whose summit potentials did not correspond to their $E_{\frac{1}{2}}$ values but instead appeared at potentials at which discharge began. Further, in contrast to cathodic waves, the anodic processes interfered with each other, the wave heights being reduced by the discharge of compounds at more negative potentials.

Organic compounds were also studied by Breyer and co-workers (1, 2). Most organic compounds are polarographically irreversible as judged by the slope of the $\log(i_d-i)/i$ plots, yet give very good a-c. waves. This is probably due to reversible steps in an over-all irreversible process. Organic compounds are detectable at lower concentrations than are inorganic by the a-c. polarographic method. For example chloranilic acid may be detected as low as 10^{-7} M and methylene blue down to 10^{-6} M. The peaks are usually within ± 50 mv. of the $E_{\frac{1}{2}}$ values. The peak heights plotted against concentration are not straight lines as with inorganic compounds but rise sharply at low concentrations and less sharply as the concentration increases finally approaching a limiting value which is apparently determined by the available electrode surface. These facts indicate that the mechanism of the a-c. polarographic oxidation and reduction of organic compounds is different from that of inorganic.

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The advantages of a-c. over d-c. polarography are as follows:

(1) There is no direct interference from dissolved oxygen.

(2) Small amounts of some compounds may be determined in the presence of large amounts of more easily reduced materials.

(3) There is a generally increased sensitivity.

(4) Polarographic waves only 40 mv. apart are clearly separable.

(5) A single measurement at the summit potential can give both $E_{\frac{1}{2}}$ and concentration of the depolarizer.

The greatest advantage of this method would be realized by its use in conjunction with d-c. polarography and it is therefore the purpose of this paper to describe a method of converting a conventional d-c. recording polarograph to one which will produce both a-c. and d-c. polarograms.

APPARATUS

The apparatus as described by Breyer, Gutman, and Hacobian (5, 7) consists of the usual polarographic circuit with the alternating voltage introduced across resistance R_2 (Fig. 2(*a*)). The galvanometer which is connected across

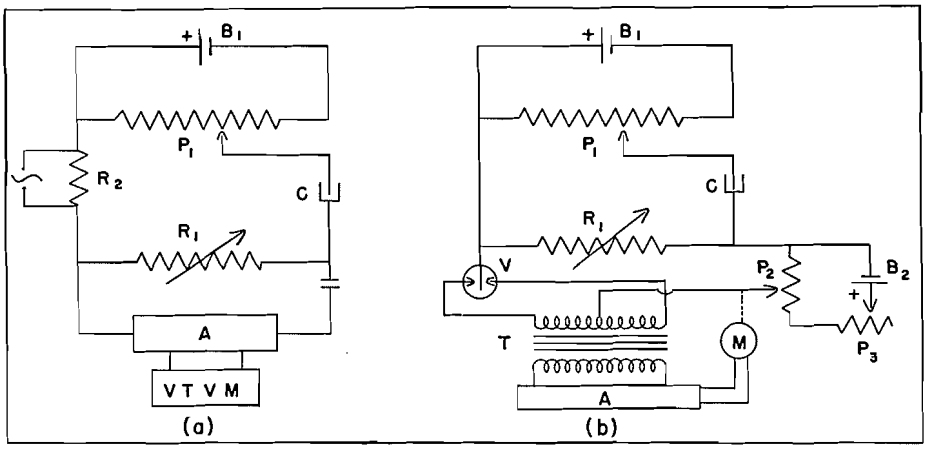

FIG. 2. (*a*) Circuit of a-c. polarograph. (*b*) Circuit of d-c. recording polarograph.

P_1, P_2, P_3—Potentiometers
C —Polarograph cell
A —A-c. amplifier
R_1—Sensitivity selector
V—Vibrator-converter
M—Balancing motor
$VTVM$—Vacuum tube voltmeter

R_1 in d-c. polarography is replaced by a condenser coupled a-c. amplifier and vacuum tube voltmeter which measures only the a-c. current passing through the circuit.

In the present report reference will be made to the Sargent Model XXI Visual Recording Polarograph, but the general methods of modifying this machine should be adaptable to all those which employ a self-balancing potentiometer type recorder utilizing a 60 cycle vibrator-converter and a-c. amplifier.

Fig. 2(*b*) is a schematic circuit diagram of this polarograph as employed in d-c. work. It is similar to that of a manual polarograph, with the exception that the galvanometer has been replaced by a resistor R_1 and recording poten-

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tiometer in parallel. The current flowing through the circuit develops a potential across R_1 which is measured by the recorder.

The recorder opposes the unknown e.m.f. across R_1 with a known e.m.f. determined by the position of the sliding contact on calibrated slide-wire P_2. Any difference in e.m.f. between R_1 and P_2 (error signal) is converted to a 60 cycle a-c. voltage by the vibrator V, amplified, and fed into the motor M which then operates the slide-wire in such a direction as to eliminate the difference. The slide-wire is calibrated periodically by reference to a standard cell, to correct for voltage changes in B_2, and any adjustments required made by means of auxiliary potentiometer P_3.

To measure the alternating voltage developed across R_1 when a-c. polarography is employed, B_2 must be replaced by an a-c. source 180° out of phase with the voltage across R_1. Since the error signal is already a-c., the vibrator is no longer necessary and is shorted out. This is the basis of the conversion, and with reference to Fig. 3 the actual details follow.

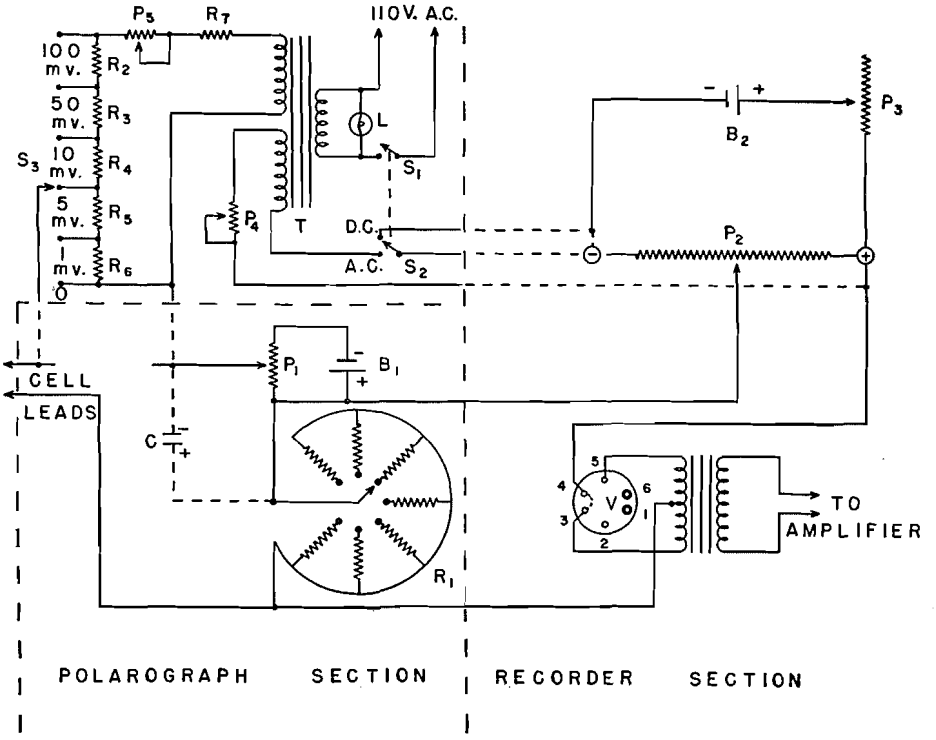

FIG. 3. Wiring diagram for a-c.–d-c. recording polarograph.

C —300–500 μf., 25 W.V.
R_1—Sensitivity selector
R_2—5.0 ohm precision
R_3—4.0 ohm precision
R_4—0.5 ohm precision
R_5—0.4 ohm precision
R_6—0.1 ohm precision
R_7—200 ohm
P_1—Polarograph slide-wire
P_2—Recorder slide-wire
P_3—Recorder balancing resistor
P_4—5000 ohm
P_5—100 ohm
S_1–S_2—DPST switch
S_3—mv. selector switch
V—Vibrator shorting plug
L —110 v. pilot light
T —Hammond 165 X 115 v. primary, 2.5–2.5 v. secondary

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The polarograph is housed in a case consisting of two parts, the upper part containing the recorder section, and the lower part the batteries and polarograph section. The a-c. components are located in the lower part outside the polarograph section with controls S_1, S_2, S_3, P_4, and pilot light L mounted on the front of the polarograph below the control panel. P_5 and R_7 are mounted behind these and the transformer is mounted behind the polarograph section near the main power inlet. The a-c. switch S_1 must be on the ungrounded side of the line to ensure that the primary of the transformer is at ground potential when operating on d-c.

The two leads entering the polarograph section do so through a terminal strip. These leads, and all leads added to the polarograph and recorder section, are shown as dotted lines in Fig. 3. A 300 μf. condenser shunts the a-c. signal around P_1 to prevent increasing the resistance to the a-c. as the resistance of P_1 is increased.

Shielding the three leads from the controls to the recorder section does not appear to be essential but is advisable. A six-prong male plug with a shorting wire between terminals 3 and 4 is used to replace the vibrator when operating the polarograph on a-c.

In wiring the transformer the recorder supply is connected first, connections being reversed if the recorder will not read zero with an open cell circuit. The other secondary is connected up in such a way that the recorder needle moves up the scale when the cell leads are momentarily shorted.

Calibration

Since the usual convention is to express a-c. voltage and current in r.m.s. terms switch S_3 reads in mv. r.m.s. The most convenient method of calibration is by means of a calibrated oscilloscope. S_3 is set at "10 mv." (the most commonly used range) and with S_1–S_2 at "a-c.", damping switch "off", and "D.M.E." switch "negative", P_5 is adjusted until a peak to peak voltage of 28.2 mv. is observed on the oscilloscope attached to the cell leads. (If P_5 is mounted behind the panel, the polarograph section must be lifted out for this operation. It may be mounted, however, on the panel as a screw adjustment.) Once adjusted P_5 should require no further attention.

Calibration of the recorder to read in μa. r.m.s. must be made after each use on d-c. This is due to the fact that P_3 is changed by the recorder as the e.m.f. of B_2 alters because of age or replacement. This is easily accomplished by plugging a 1000 ohm precision resistor into the cell lead jack, setting S_3 at "10 mv.", sensitivity at "0.100 μa./mm.", damping switch "off", operation switch at "e.m.f. constant", and adjusting P_4 to give a difference of 100 mm. between "D.M.E." switch "off" and "negative".

Operation

The change from a-c. to d-c. operation is made by putting switch S_1–S_2 at "a-c." and replacing the vibrator in the amplifier by the shorting plug. The normal d-c. polarographic controls apply to a-c. operation as well except for the damping switch which must be "off" during a-c. polarography.

A comparison of a-c. and d-c. polarograms was made using a mixture of six ions in 0.5 M HCl. Fig. 4 shows the actual polarograms obtained and demon-

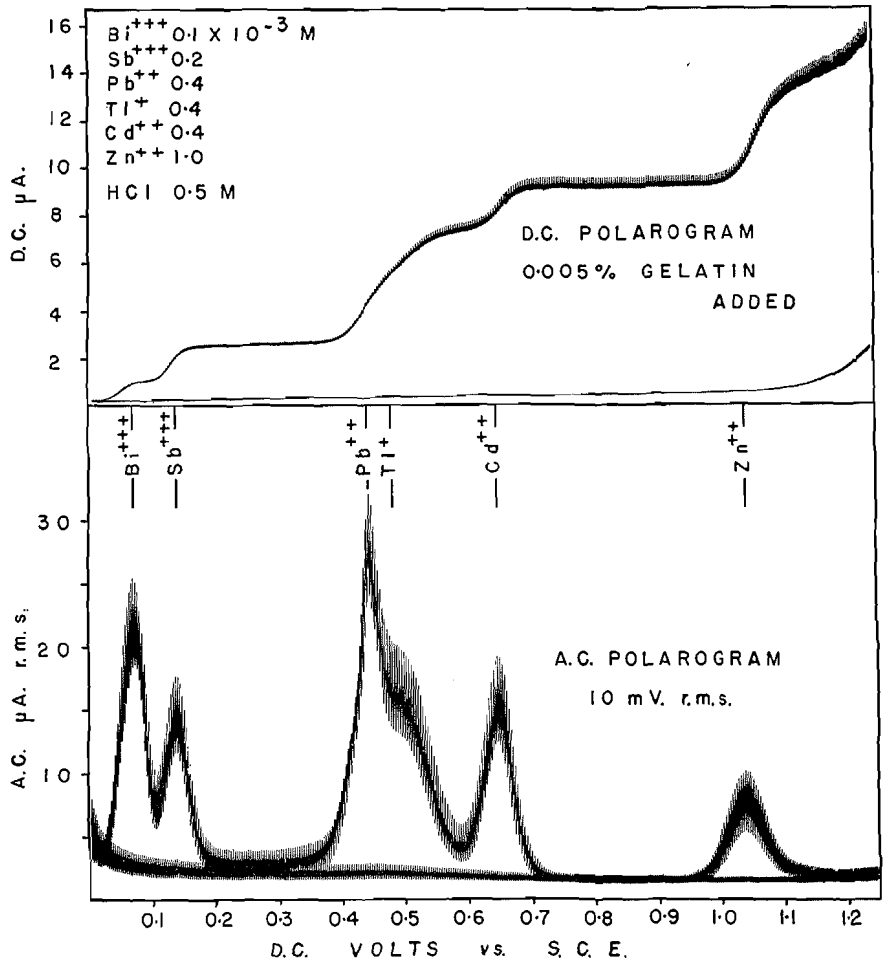

FIG. 4. A-c. and d-c. polarograms of a mixture of ions.

strates the essential advantages of a-c. over d-c. polarography, i.e. increased sensitivity, less interference between waves (Tl^+ much more obvious), E_s more readily measured than $E_{\frac{1}{2}}$, no interference from oxygen (present in the a-c. polarogram).

In general it is felt that the small amount of effort needed to modify the polarograph is more than repaid in increased versatility.

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GRAFT COPOLYMERS OF STYRENE AND METHYL METHACRYLATE

PART I: SYNTHESIS[1,2]

By M. H. Jones

ABSTRACT

A series of graft copolymers of styrene and methyl methacrylate have been prepared by using samples of brominated polystyrene as photochemical initiators for the polymerization of methyl methacrylate. Estimates of the branch chain lengths have been obtained from kinetic and viscosity measurements. In conjunction with the infrared analyses of the total weights of the branches, these have permitted a determination of the frequencies of branching.

INTRODUCTION

There has been considerable interest of late in the preparation of copolymers in which the respective monomer units are arranged in discrete blocks within the polymer molecule rather than distributed randomly. In general, two types of 'block' copolymers can be prepared; that in which two or more groups of repeating monomer units are arranged within a linear molecule and, the second, in which branches of a different monomer are grafted onto the backbone of a homogeneous polymer chain. Obviously there are variants in which the two types of structure can be combined. This paper is concerned with the synthesis of the second kind, namely graft copolymers of styrene and methyl methacrylate of which styrene units comprise the backbone of the molecule and the branches are composed of methyl methacrylate units.

It is probable that branching occurs in a normal radical polymerization through the abstraction of a hydrogen atom from a dead polymer molecule or a growing polymer chain, the resultant radical acting as an initiator for polymerization in the monomer with the growth of a branch. As the activation energy of such a transfer step is generally considerably greater than that of propagation, branching will only become significant at high temperatures or at high conversions when the concentration of polymer is appreciable. Evidence of grafting by transfer in certain systems has been obtained by polymerizing monomers in the presence of large concentrations of a foreign polymer (3, 7, 11, 15). The method has certain disadvantages in that large amounts of homopolymer are formed and, when grafting is small, the product may contain three constituents, an unbranched residue of the initial polymer, the graft material, and the homopolymer produced during polymerization.

An alternative means of grafting involves the use of a polymer containing active groups or atoms distributed along its chain as an initiator for polymerization. Elimination of these groups in the presence of a monomer, either thermally or photochemically, will provide radical centers in the polymer chain at

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Contribution from the Department of Chemistry, Ontario Research Foundation, Toronto 5, Ontario.
[2]*Presented at the 6th Canadian High Polymer Forum held at St. Catharines, Ontario, April 14–15, 1955.*

which polymerization can start with the growth of branches. It must be supposed that the atoms or radicals produced simultaneously will also initiate polymerization in the monomer and the product will consist of a mixture of graft copolymer and linear homopolymer. As the frequency of branching can be controlled more easily by this method, conditions can be chosen such that all the initiating polymer molecules are branched. In the present work, samples of brominated polystyrene have been used for photochemical initiation (9, 10). Recently, polymethyl vinyl ketone (5, 6), polymethyl acrylates containing per-ester groups (13), and alkylated polystyrene hydroperoxides (12) have all been used as polyradical sources for the synthesis of graft copolymers.

EXPERIMENTAL

Materials

Methyl methacrylate (Matheson, Coleman, and Bell Practical Grade) was shaken three times with 5% solutions of sodium hydroxide to remove the inhibitor, washed with distilled water, and dried over anhydrous sodium sulphate. The product was distilled in an atmosphere of nitrogen at 110 mm. pressure. The second fraction, b.p. 47.0–47.2°C. was retained for the polymerization experiments and given a bulb-to-bulb distillation in vacuum prior to use. The benzene and carbon tetrachloride used as solvents were of reagent grade quality and were dried and distilled before use. For the fractionation experiments, reagent grade methanol was used without further purification.

Procedures

Polymerizations were carried out in calibrated pyrex dilatometers having bulb diameters of 15 mm. and capacities of approximately 12 cc. The dilatometers were sealed to suitable bulbs into which was weighed the brominated polystyrene. The system was evacuated on a high vacuum line and known volumes of the monomer and solvent distilled in from calibrated burette stems. After the mixture had been thoroughly degassed, the system was sealed under vacuum. When the polymer had dissolved, the dilatometer was filled by tipping and sealed off at the end of the capillary.

The photochemical polymerizations were conducted in a thermostat bath at 25.0°C±0.005°C. The windows of the bath were also of pyrex. A General Electric mercury lamp (Type H100-A4) with the envelope removed was used as the light source and the beam was roughly collimated by a quartz lens. The reactions were followed by observing the fall in level of the meniscus in the capillary by a cathetometer. Rates were calculated on the assumption that a contraction in volume of 23.1% corresponds to 100% polymerization (14). At the end of a reaction, the mixture was diluted with benzene to give a 1% polymer solution and the polymer precipitated by dropwise addition to a 30-fold excess of methanol. Polymers were dried to constant weight on a high vacuum line at room temperature and the recoveries obtained were 92–95% of the theoretical.

The reaction products, which consisted of graft copolymer and polymethyl methacrylate, were separated by fractional precipitation using the solvent–

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precipitant system benzene–methanol. The precipitant was added slowly to a solution of the polymer mixture (approximately 0.8 gm./100 cc.) at 25°C. until the first sign of gel formation was observed. A known volume of methanol was added in excess, the solution was warmed 10°C. to redissolve the gel and allowed to cool slowly to thermostat temperature. After a period of 18 hr. to allow the gel to settle, the supernatant solution was carefully decanted, the gel dissolved in benzene and reprecipitated. Successive fractions were obtained in a similar manner. The fractions collected before the inflection point of the fractionation curve were assumed to consist of the graft copolymer. To remove small amounts of polymethyl methacrylate which remained as the result of 'tailing', these fractions were combined and reprecipitated as a single fraction at the benzene–methanol composition corresponding to the inflection point of the curve.

The compositions of the individual polymer fractions were determined by infrared analysis using the strong carbonyl absorption band of the polymethyl methacrylate at 1733 cm.$^{-1}$. Trichloroethylene was used as the solvent for these measurements and the compositions were obtained from the optical densities by comparison with a calibration curve prepared from synthetic mixtures of polystyrene and polymethyl methacrylate. Duplicate analyses agreed within 2%. As a check on the analytical values, measurements were also made on the phenyl absorption band of the polystyrene residue at 699 cm.$^{-1}$ where polymethyl methacrylate is transparent.

Viscosity measurements were made in benzene solution at 25°C. with a Ubbelohde type viscometer incorporating a large bulb to permit dilution of the solution *in situ*.

Bromination of Polystyrene

Samples of brominated polystyrene for use as polyradical sources were prepared by the photobromination of a high molecular weight polystyrene. This method was chosen to ensure that substitution occurred preferentially in the carbon chain of the molecule. The starting material, which was believed to have little or no branching, was prepared by thermally polymerizing styrene at 70°C. to a conversion of 10%. Solutions of this polymer (1–2%) in carbon tetrachloride containing various amounts of bromine were degassed, sealed under vacuum, and irradiated with ultraviolet light at 25°C. until the intensity of the bromine color decreased by approximately 50%. Irradiation times were usually 15–20 min. The incident radiation was limited to the wave length region 3500–4800 Å by a Corning Glass filter No. 5113 to reduce any simultaneous photolytic decomposition of the product. At the end of a reaction, the volatile components were removed by vacuum distillation at room temperature and the brominated polystyrene recovered by dissolving in benzene and reprecipitating from methanol. These polymers show a marked increase in absorption over polystyrene in the region 2800–3500 Å. The bromine contents and intrinsic viscosities of various samples are recorded in Table I. The molecular weights given in the last column of this table were derived from the intrinsic viscosity – molecular weight relationship of Ewart and Tingey (4) for unfractionated polystyrenes, i.e. $[\eta] = 0.75.10^{-4}\ M_n^{0.783}$. It is apparent that the bromination

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TABLE I

PHOTOBROMINATION OF POLYSTYRENE

Sample No.	% Br	$[\eta]_{25°C.}$	$M_n.10^{-3}$
Original polystyrene	—	3.16	810
A	2.15	1.30	260
B*	3.18	0.84	150
C	3.85	1.60	340
D	2.60	1.55	325
E	3.16	1.84	400

**Prepared by thermal bromination at 60°C.*

reaction is accompanied by some degradation of the polymer. Attempts to prepare polystyrenes containing aliphatic bromine atoms by copolymerization of styrene with α or β bromostyrene proved unsuccessful (8).

Grafting Reactions

For the grafting reactions, benzene was added as a diluent to reduce the rate and chain length of the branches. All the graft copolymers were soluble in

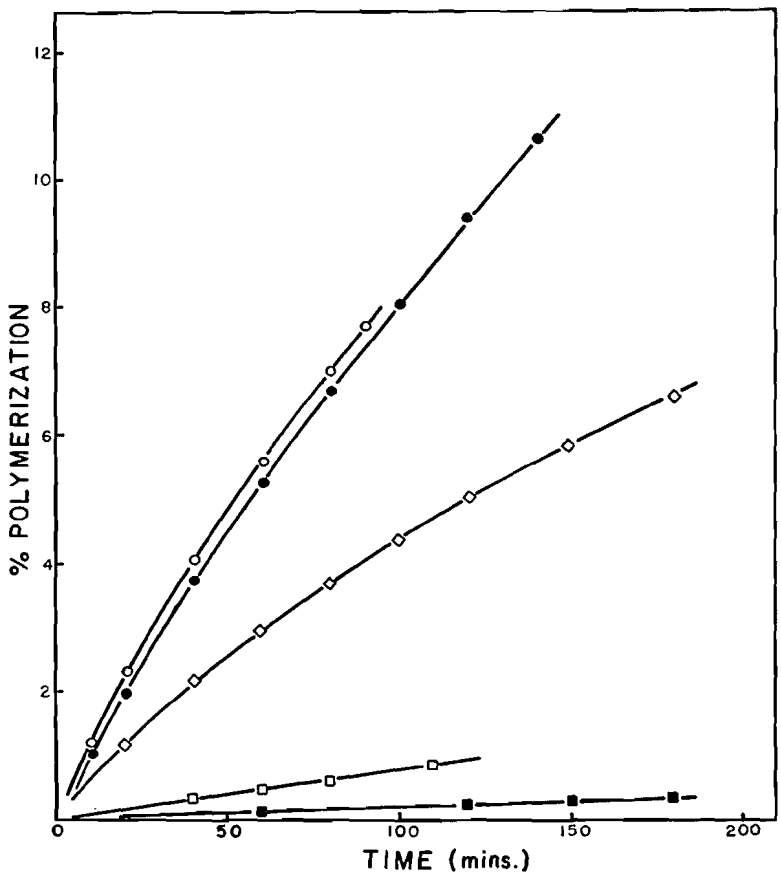

FIG. 1. Reaction–time curves for grafting experiments.
Expt. No. D2, -○-; Expt. No. E3, -●-; Expt. No. A1, -◇-; Pure monomer, no filter, -□-; Pure monomer, filter 584, -■-.

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benzene although those with higher degrees of branching dissolved with some difficulty. During polymerization, the radical termination process must, therefore, be mainly disproportionation since termination of growing chains by a combination mechanism would result in cross-linking with the formation of an insoluble network. This condition was observed in branching reactions with styrene (9, 10). Using radioactive initiators, Bevington, Melville, and Taylor (2) have demonstrated that disproportionation occurs twice as frequently as combination in methyl methacrylate polymerization at 25°C.

Typical reaction–time curves for the grafting experiments are shown in Fig. 1 and it is apparent that the rate decreases with extent of polymerization. The rates recorded in Table II are the mean values determined from the total dilatometric contractions. For the series of experiments E1–E4, where polymerization conditions were identical except that successive reactions were allowed to go to higher conversions, a decrease in the average rate of 35% was observed. The cause of this is not known. It cannot be attributed to impurities in the monomer as the contraction–time curves when α,α'-azo-bis-isobutyronitrile was used as initiator showed no deviations from linearity up to conversions of 10%. In addition, in similar branching experiments with styrene (10), the rate was also independent of the extent of reaction.

TABLE II

PHOTOCHEMICAL POLYMERIZATION OF METHYL METHACRYLATE AT 25°C. INITIATED BY BROMINATED POLYSTYRENE

Expt. No.	[Polymer], gm. dl.$^{-1}$	[Monomer], moles l.$^{-1}$	Rate. 10^6, moles l.$^{-1}$ sec.$^{-1}$	% Conversion	$\bar{P}_n$ (kinetic)	$[\eta]_{25°C}$, dl. gm.$^{-1}$	$\bar{P}_n$ (viscosity)
Pure monomer*	—	9.32	2.85				
Pure monomer	—	9.32	11.6				
A1*	1.42	9.19	57	7.11	4900	1.60	4500
A2*	1.40	2.91	9.4	17.8	3100	0.590	1450
D1	1.52	9.18	150	5.75	2050	0.890	2300
D2	1.55	7.14	104	7.87	1800	0.695	1750
D3	1.62	5.11	59	11.2	1650	0.640	1600
D4	1.50	3.00	27	17.5	1250	0.530	1300
E1	1.46	6.68	115	3.72	1450	0.615	1550
E2	1.46	6.68	95	7.43	1700	0.610	1550
E3	1.46	6.68	85	11.2	1900	0.710	1800
E4	1.46	6.68	80	16.4	2050	0.750	1900

**Corning filter No. 5840 used. Incident radiation limited to wave length region 3100–4000 Å.*

If it is assumed that the brominated polystyrene functions solely as an initiator, the mean degree of polymerization, which is also the chain length of the branches, can be calculated from the measured rate of reaction and the kinetic constants available in the literature. From the usual kinetic scheme for vinyl polymerization, it can be shown that the degree of polymerization can be related to the rate of reaction by the expression

$$1/\bar{P} = k_t/k_p + k_t R/k_p^2[M]^2$$

where k_p, k_t, and k_t are the rate coefficients of propagation, termination, and transfer. The chain lengths recorded in Table II were calculated from the above

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expression using values of 3.10^{-5} and 260 for k_t/k_p and k_t/k_p^2 respectively (2).

As mentioned previously, the bromine atoms formed in the photochemical step also initiate polymerization in the monomer with the formation of polymethyl methacrylate whose average length should be identical with that of the branches grafted onto the polystyrene chain. Consequently a second method of determining branch length is available. The intrinsic viscosities of the total polymethyl methacrylates recovered from each reaction mixture by fractionation are also given in Table II together with the number average chain lengths derived from the viscosity – molecular weight relationship of Baysal and Tobolsky (1), i.e. $[\eta] = 9.4.10^{-4}\,\bar{P}_n^{0.885}$. The agreement between the values obtained by the two independent methods is surprisingly good.

Isolation and Analysis of the Graft Copolymers

Two typical fractionation curves of the products from grafting reactions, in which the total percentage of polymer recovered is plotted as a function of the methanol content of the solution, are shown in Fig. 2, together with a

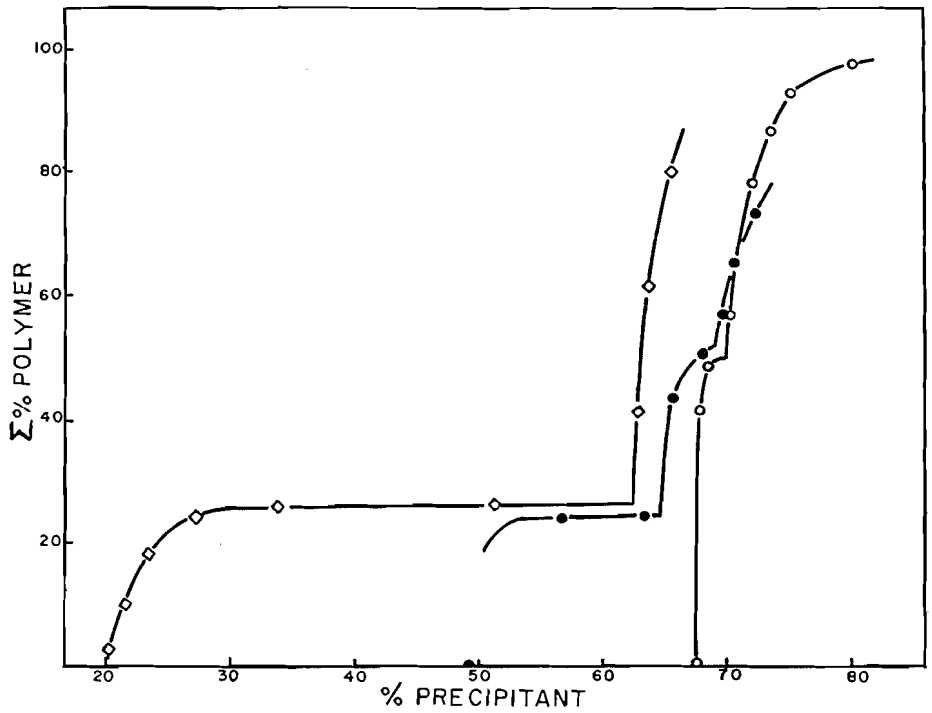

FIG. 2. Fractionation curves.
Expt. No. A1, –○–; Expt. No. E3, –●–; Synthetic mixture containing 26.9% of brominated polystyrene C, and 73.1% polymethyl methacrylate, –◇–.

curve of a synthetic mixture of brominated polystyrene and polymethyl methacrylate. The latter has been displaced five units to the left in the ordinate scale for clarity. The double inflection in experiment E3 was also observed in the fractionations of other graft copolymers with high degrees of branching.

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Probably this initial coagulation represents a nonequilibrium condition resulting from the intertwining of branched polymer chains with the formation of aggregates. These first fractions were always precipitated as more highly swollen gels than later ones although the analysis values were the same. There is an alternative explanation. If, under the conditions of the branching reactions, a fraction of the growing branches terminate by a combination mechanism (2) some cross-linking will occur as the frequency of branching increases with the formation of molecules having two or three times the molecular weight of the average. As this would create a distinct discontinuity in the molecular weight distribution, the solubility curve would also be discontinuous. However, the comparatively crude fractionation method employed is not usually capable of separating molecular weight species of this order.

During the fractionation experiments, an interesting solubility phenomenon was observed. Within the solvent–precipitant range where polystyrene usually precipitates, the solutions became opaque although no coagulation and gel formation occurred. They were quite stable, could be kept for several days without change, and even centrifuging at moderate speeds (up to 5000 r.p.m.) only partly coagulated the suspended polymer. In this solubility range, it appears that the graft copolymer molecules behave in a manner somewhat analogous to a micelle. Presumably the precipitant causes desolvation of the polystyrene part of the molecule, with a partial collapse of the polymer segments, while the polymethyl methacrylate branches remain solvated and thus prevent coagulation. The same type of behavior was noted by Merrett (11) with copolymers composed of polymethyl methacrylate branches grafted onto rubber.

In Fig. 3, the methyl methacrylate compositions of the individual polymer fractions have been plotted as a function of their cumulative mean weight percentages for a series of experiments with increasing amounts of branching. The analyses of successive copolymer fractions remained sensibly constant except where the frequency of branching was small. The lower values in the first fractions of these examples may be due to contamination with small amounts of the initial brominated polystyrene which remained unbranched. As this material has a lower solubility than either the copolymer or polymethyl methacrylate, it will coprecipitate with the first fraction. That contamination is not a serious factor was demonstrated by a fractionation experiment with a synthetic mixture of graft copolymer and brominated polystyrene in which at least 90% of the latter was recovered. In addition, when the frequency of branching is low, the large solubility differences between molecules with consecutive numbers of branches may give a similar trend.

The fractionation experiments also provide an alternative method to infrared analysis of estimating the compositions of the copolymer samples. Assuming that the inflection point in a fractionation curve corresponds to the separation of graft and linear polymer, the composition can be determined from the total weight of graft copolymer and the corresponding weight of brominated polystyrene used as initiator. The agreement between the two methods is within the experimental accuracy (Table III). From the weight

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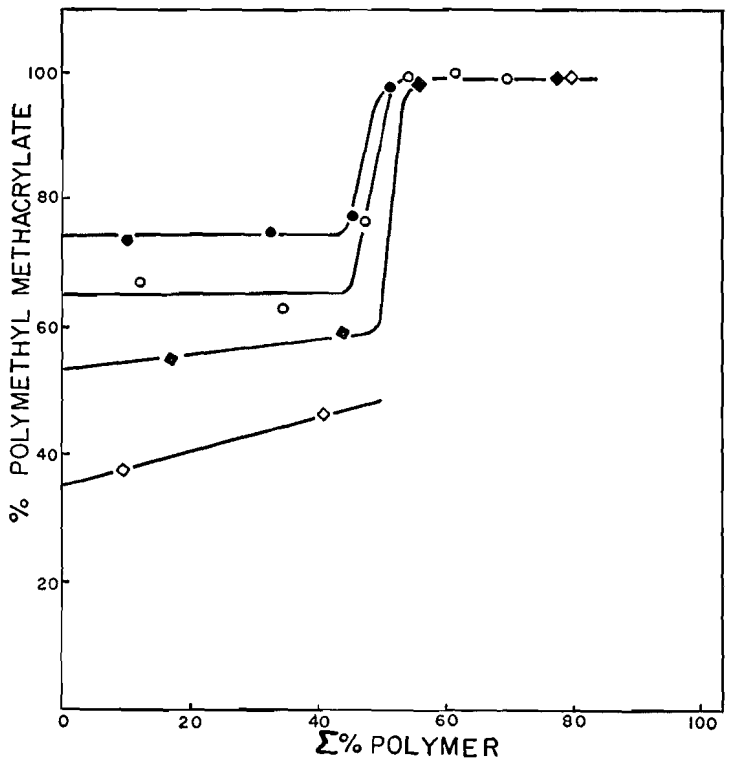

FIG. 3. Plot of polymethyl methacrylate composition versus total weight of polymer recovered.
Expt. No. E1, –◇–; Expt. No. E2, –◆–; Expt. No. E3, –○–; Expt. No. E4, –●–.

TABLE III

GRAFT COPOLYMERS OF STYRENE AND METHYL METHACRYLATE

Expt. No.	% PMMA (fractionation)	% PMMA (infrared)	$\bar{P}_n$ (styrene backbone)	$\bar{P}_n$ (methacrylate branches)	Monomer units of backbone per branch	Average no. of branches per molecule
A1	64	67	2500	4500	2100	1.2
A2	49	47	2500	1500	1700	1.5
D1	63	66	3100	2300	1200	2.6
D2	65	65	3100	1700	900	3.4
D3	62	60	3100	1600	1000	3.0
D4	59	58	3100	1300	920	3.3
E1	41	41	3800	1500	2100	1.8
E2	57	55	3800	1500	1200	3.2
E3	68	64	3800	1800	950	3.9
E4	75	74	3800	1900	650	5.9

fraction of the branches and their average chain length, a simple calculation yields the frequency of branching. The complete data for a number of graft copolymers are given in Table III. The copolymer compositions determined by infrared analysis were used in the calculations as these were considered

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more reliable. In the series of experiments E1–E4, the polymerization conditions were kept constant and increasing amounts of branching were obtained by allowing the reactions to go to progressively higher conversions. Because of the decrease in polymerization rate with extent of reaction, there is also a small increase in the chain lengths of the branches for the series.

The methods that have been described for the synthesis and characterization of graft copolymers of styrene and methyl methacrylate should be of general applicability.

ACKNOWLEDGMENTS

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MOLECULAR INTERACTION OF HYDROGEN CHLORIDE WITH π-ORBITAL DONOR MOLECULES

I. ALKENES AND ALKYNES[1]

By D. Cook,[2] Y. Lupien, and W. G. Schneider

ABSTRACT

Hydrogen chloride, which is a convenient small molecule "acceptor", was used to study the donor capacity of π-orbitals in a number of ethylenic and acetylenic hydrocarbons. The composition of the molecular addition compounds formed between these hydrocarbons and hydrogen chloride was determined by thermal analysis. The freezing-point diagrams for hydrogen chloride with a number of lower alkene homologues and with several alkyne homologues are reported. The addition compounds formed by the alkenes have HCl:hydrocarbon molecular ratios of 1:1 and 2:1. An exception is 2-methyl-butene-2 which undergoes rapid chemical reaction with HCl even at low temperatures. The HCl-complexes formed by the alkynes have molecular ratios 1:1, 2:1, and 4:1. Addition compounds of this type are not formed by the saturated hydrocarbons ethane and propane and therefore they must be attributed to specific forces of interaction of HCl with π-orbitals of the unsaturated hydrocarbons. It is suggested that weak hydrogen bonds are formed between the acid acceptor and the donor π-orbitals. To account for the 2:1 complex in the alkenes and the 4:1 complex in the alkynes it is necessary to postulate that each π-orbital can accommodate two molecules of HCl.

INTRODUCTION

Molecules containing either lone pair orbitals or π-orbitals frequently have a highly directed intermolecular force field and may accordingly associate or form molecular complexes with other molecules. Generally speaking, a lone pair orbital is localized on one atom of the molecule from which it projects out into space as a well-defined region of negative charge. Accordingly such molecules are usually polar and they are good electron donors capable of complex formation with an acidic or acceptor molecule. A common example of complexes of this type is the hydrogen bond. A π-orbital, on the other hand, while it also represents a directed region of negative charge on the molecule, is usually not as well localized and consequently does not project out as far from an atom center as a lone pair orbital. Moreover because of its symmetry a π-orbital does not impart a "polar" character to the molecule. Nevertheless one should expect π-orbitals to have a definite, although weaker, donor property and hence to be capable of forming a variety of molecular complexes, including perhaps a weak hydrogen bond.

In this connection it was of some interest to study the donor capacity of the π-orbitals in olefins and acetylenic compounds. The technique employed for this purpose was that of thermal analysis. In order to ascertain what molecular complexes these hydrocarbon molecules form with a simple acceptor (acid) molecule like hydrogen chloride the freezing-point diagram of the binary

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Contribution from the Division of Pure Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 3983.
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mixture was determined. For this purpose hydrogen chloride may be regarded as a "probe" molecule. It is a small molecule and a strong acceptor and hence we may assume that if we add sufficient hydrogen chloride (and if the temperature is not too high) all the donor centers of a given molecule will be saturated. Thus, one may expect that the molecular compound appearing in the freezing-point diagram with the greatest hydrogen chloride content will give an indication of the maximum number of active donor centers in a given molecule. The use of hydrogen chloride as a test molecule has a further advantage. Some of the molecular complexes may be expected to be weak. Since hydrogen chloride has a low melting point it is possible to work at low temperatures, and under these conditions even weak complexes may be expected to show up in the freezing-point diagram.

EXPERIMENTAL

The freezing-point cell employed in the present work was similar to that used previously (2). It was joined to a high vacuum system in which known amounts of pure dry hydrogen chloride gas could be measured volumetrically and subsequently condensed into the freezing-point cell cooled with liquid nitrogen. The amount of hydrocarbon in each mixture was obtained either by volumetric measurement or, in the case of liquid hydrocarbons, by weighing from a weighing bulb which could be attached to the vacuum system. The hydrocarbons employed were Phillips "Research Grade" chemicals. Temperatures were measured with a copper–constantan thermocouple. Cooling curves were recorded with a Leeds and Northrup "Speedomax" recorder.

RESULTS

The freezing-point diagrams of hydrogen chloride with some simple alkenes are shown in Fig. 1 and those with some alkynes in Fig. 2. In these diagrams vertical dotted lines indicate the composition of the molecular compounds formed, horizontal dotted lines are eutectic lines, and curved dotted lines are the hypothetical melting curves of incongruently melting compounds. Duplicate cooling curves were obtained for each mixture and each composition was repeated with a fresh mixture. The melting points were reproducible to $\pm 1.0°C.$, the estimated accuracy of the measurements.

The compositions and melting points of the molecular compounds formed are summarized in Table I. Ethylene, propylene, and *cis*-butene have similar freezing-point diagrams in that they all show two compounds containing one and two molecules of HCl respectively, per molecule of olefin. In this respect *trans*-butene appears somewhat anomalous in that, while a 2:1 compound (two molecules of HCl per molecule of olefin) is present, the 1:1 compound is not evident. Actually the absence or presence of the latter compound in the HCl–*trans*-butene system may be somewhat doubtful. If it does exist it would be expected to melt incongruently because of the high melting point of *trans*-butene itself. Moreover, mixtures of *trans*-butene (as well as *cis*-butene) with HCl showed a marked tendency to supercooling and glass formation which was

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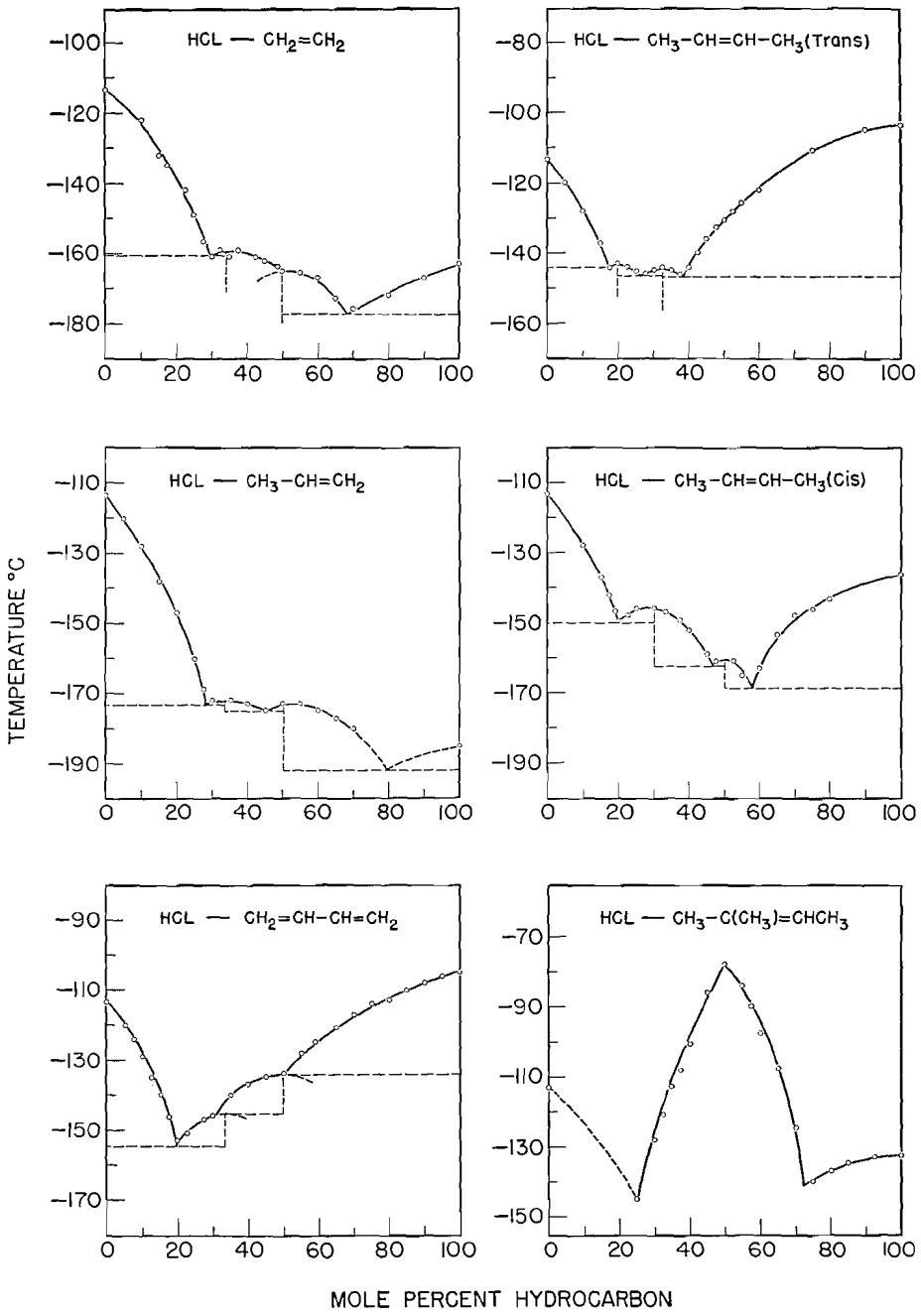

FIG. 1.

particularly pronounced in mixtures containing between 50 to 80 mole per cent of hydrocarbon. Consequently the freezing-point diagram in this composition range has a somewhat greater uncertainty. *trans*-Butene also differs from the

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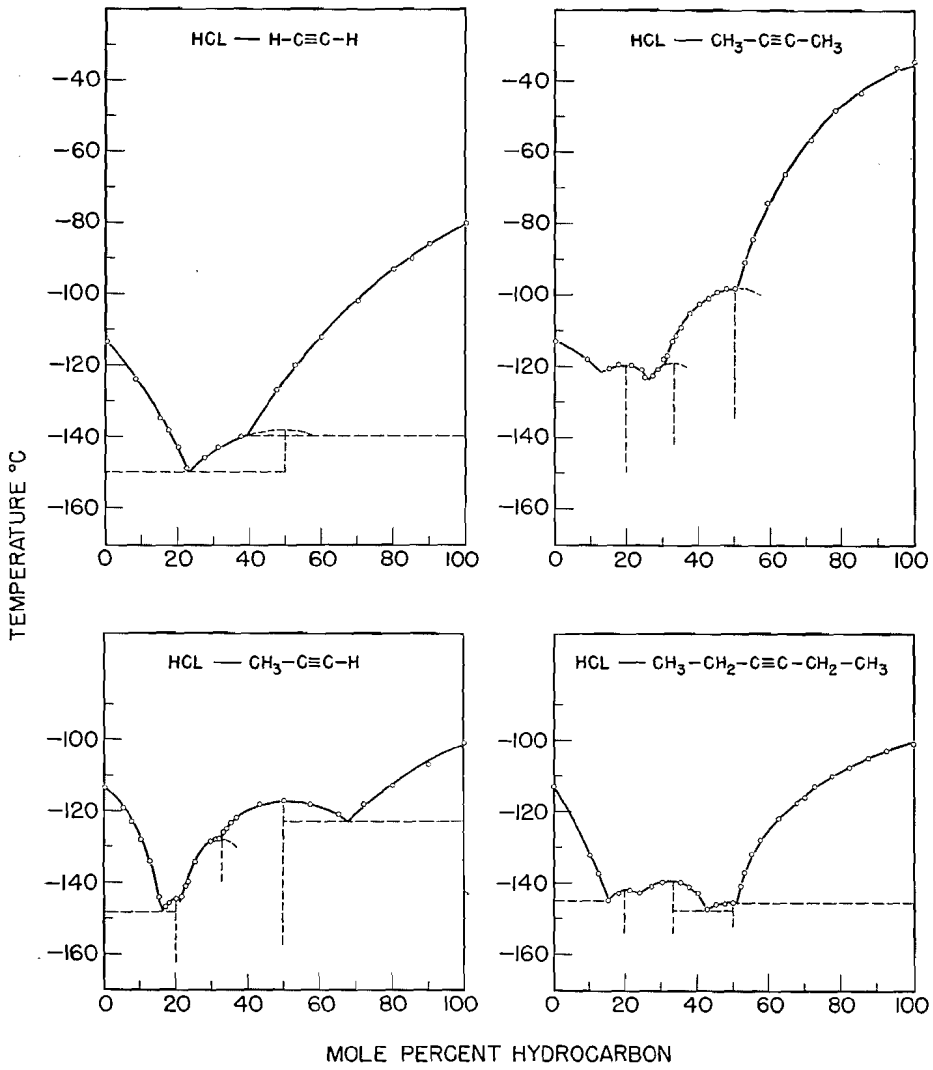

FIG. 2.

other three olefins in that an additional compound with composition 4:1 appears in the freezing-point diagram.

The freezing-point diagram of 2-methyl-butene-2 is strikingly different from the above-mentioned olefins. It shows a very pronounced (stable) 1:1 compound. This type of diagram results when instead of molecular compound formation a chemical compound is formed. Chemical addition of HCl across the double bond was verified by measuring the proton magnetic resonance spectrum of the product, 2-methyl-2-chloro-butane, and comparing this with the spectrum of the parent olefin. It is curious why HCl addition, which appears to be almost instantaneous, takes place so readily for this particular

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TABLE I

SUMMARY OF HYDROGEN CHLORIDE MOLECULAR COMPOUNDS

Hydrocarbon	Compound, HCl:hydrocarbon	Melting point* (°C.)
Ethylene	1:1	−165
	2:1	−159
Propylene	1:1	−172
	2:1	−173
cis-Butene-2	1:1	−160
	2:1	−145
trans-Butene-2	2:1	−143
	4:1	−139
Butadiene	1:1	−135
	2:1	−145 (*i*)
Acetylene	1:1	−137 (*i*)
Propyne	1:1	−117
	2:1	−128 (*i*)
	4:1	−145
Butyne-2	1:1	− 98
	2:1	−120 (*i*)
	4:1	−119
Hexyne-3	1:1	−145
	2:1	−139
	4:1	−142

*(*i*)—*Incongruent melting point.*

olefin at temperatures below −60°C. In an attempt to eliminate possible impurities which might serve as catalysts, another sample of 2-methyl-butene-2 was distilled through an efficient fractionating column. This sample yielded identical results.

In the freezing-point diagrams for the alkynes with HCl, propyne, butyne-2, and hexyne-3 all have similar diagrams in that the compounds 1:1, 2:1, and 4:1 appear. The first member of this series, acetylene, is anomalous, forming only a 1:1 compound.

From the above results the conclusion emerges that all the unsaturated hydrocarbons studied, with the exception of 2-methyl-butene-2, form molecular complexes with hydrogen chloride. If this is a specific property of hydrocarbons containing a π-orbital it should be absent in the saturated hydrocarbons. To test this the freezing-point diagram for the propane–HCl system was determined. This is shown in Fig. 3. The freezing-point diagram of the ethane–HCl system has been previously reported in the literature (1). The phase diagrams for these two systems are similar in that they exhibit neither eutectic points nor molecular compounds. The diagrams are consistent with the assumption that the solid phase consists of a continuous series of solid solutions.

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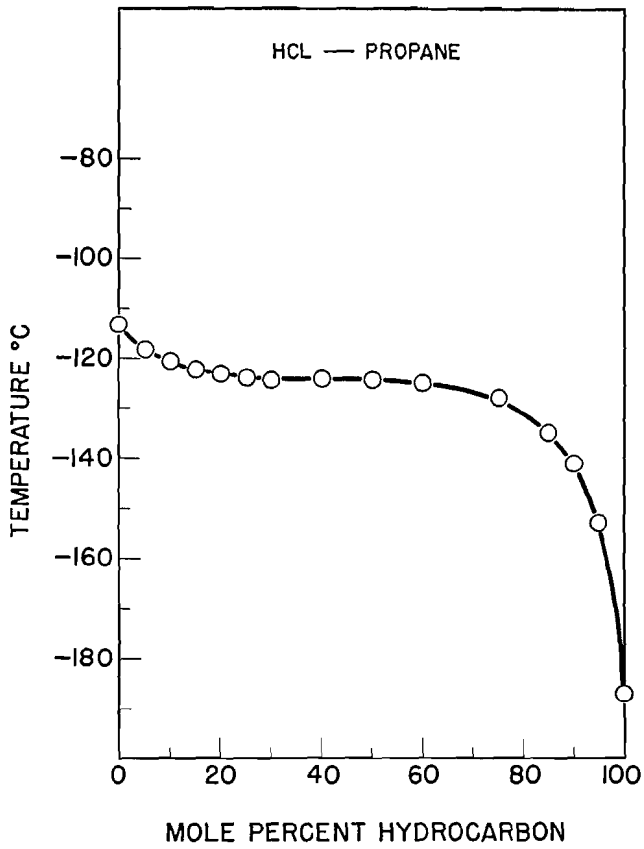

FIG. 3.

DISCUSSION

From an inspection of the molecular compounds which appear in the phase diagrams of the olefins and acetylenic compounds with HCl the following striking pattern emerges: In the olefin systems the compositions of the molecular compounds which predominate have HCl to hydrocarbon ratios of 1:1 and 2:1; for the alkynes the compounds with composition 1:1, 2:1, and 4:1 predominate. The deviations from this pattern which occur have already been mentioned. Since the same addition compounds appear for each hydrocarbon of a homologous series irrespective of the size and shape of the hydrocarbon molecule, this suggests that the compounds are in the main not due to geometrical considerations of crystal packing, but that they must be attributed to specific forces of interaction between HCl and the unsaturated hydrocarbons. This is also confirmed by the fact that the saturated hydrocarbons, ethane and propane, form no addition compounds with HCl.

The specific forces operative may be assumed to be of the donor–acceptor type in which HCl, which interacts only weakly with itself, functions as the acid acceptor. The donor centers must then be presumed to be the π-orbital

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of the unsaturated hydrocarbon. Hence in the addition compound the H atom of the hydrogen chloride is directed toward a lobe of the π-orbital. This is in effect a weak hydrogen bond. Such hydrogen bonds may be expected to be weaker than ordinary hydrogen bonds involving n-donors since π-orbitals are not as well localized as lone pair orbitals (3). Moreover if the assumption is made that each ethylenic-type π-orbital can accommodate a maximum of two HCl acceptors, one on each lobe of the π-orbital, then the composition of the addition compounds appearing in the freezing-point diagrams can be accounted for. Thus the olefins may complex with one or two molecules of HCl per molecule of hydrocarbon, while the alkynes, under favorable conditions, may accommodate up to four molecules of HCl. A similar explanation has been advanced previously (2) to account for the observed addition compounds of HCl with alkyl nitriles.

Two of the hydrocarbons studied apparently do not exhibit their maximum donor capacity relative to HCl. These are butadiene and acetylene, each of which contains two π-orbitals, and they might therefore be expected to form addition compounds containing a maximum of four HCl molecules. The π-orbitals in butadiene and other conjugated diolefins are known to be more delocalized than those of ethylene and therefore could be weaker donors. Acetylene, the first member of the alkyne series, is also a weak donor (weak base). This is indicated by its rather high ionization potential* relative to that of the higher homologues of the alkyne series and to that of ethylene.

The HCl-complexes of all the unsaturated hydrocarbons studied are relatively weak. This is evident from the general nature of the phase diagrams, the fusion curves of the addition compounds exhibiting broad, flat maxima. It is quite possible that in many cases the compounds are relatively stable only at low temperatures.

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The ionization potential can frequently be used to give a rough correlation of donor strengths of a series of compounds; the lower the ionization potential the greater the donor or basic strength.

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MOLECULAR INTERACTION OF HYDROGEN CHLORIDE WITH π-ORBITAL DONOR MOLECULES

II. BENZENE AND METHYL BENZENES[1]

By D. Cook,[2] Y. Lupien, and W. G. Schneider

ABSTRACT

Freezing-point diagrams of the binary systems consisting of hydrogen chloride with each of the hydrocarbons benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, and mesitylene were determined. The phase diagrams exhibit 1:1 complexes in each of these systems. Toluene shows an exceptional behavior in that an additional compound containing two molecules of hydrocarbon per molecule of hydrogen chloride is also formed. The 1:1 complexes are attributed to weak hydrogen bonds formed between the acid and the π-orbital donors of the hydrocarbon. Colored complexes with HCl are formed by *trans*-stilbene and anthracene. The saturated cyclic hydrocarbons cyclohexane and cyclopropane form no addition compounds with hydrogen chloride.

INTRODUCTION

The methods described in the previous paper (3) were employed to study the π-orbital donor capacity of some benzene hydrocarbons. The binary phase diagrams of hydrogen chloride with benzene, toluene, ortho-, meta-, and para-xylene, and mesitylene are shown in Fig. 1. As in the previous paper, vertical dotted lines represent the composition of the complexes formed, horizontal dotted lines being the eutectic lines. Curved dotted lines represent the hypothetical melting lines of incongruently melting complexes. As a direct result of the high melting points of benzene and *p*-xylene relative to that of HCl, these hydrocarbons form incongruently melting complexes whose composition cannot be definitely established. It is very probable, however, that the molecular ratio of HCl to hydrocarbon in the complex is 1:1, since complexes of this composition appear in all the other systems studied. Toluene exhibits a somewhat anomalous behavior. In addition to a 1:1 complex, there is a further compound containing two molecules of toluene per molecule of HCl. Table I contains a summary of the melting points of the complexes appearing in the phase diagrams.

Addition products, presumably 1:1 complexes, were also indicated for *trans*-stilbene and anthracene with HCl. Small amounts of these hydrocarbons were dissolved in anhydrous liquid HCl. *trans*-Stilbene yielded a deep blue solution and anthracene a yellow solution. Because of the high melting points of these hydrocarbons the complete phase diagram for these mixtures could not be measured with the apparatus employed for the present experiments. Such measurements could no doubt be carried out with a suitable high pressure freezing-point cell.

[1]*Manuscript received April 4, 1956.*
Contribution from the Division of Pure Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 3984.
[2]*National Research Laboratories Postdoctorate Fellow 1953–55. Present address: Dow Chemical Company, Midland, Michigan.*

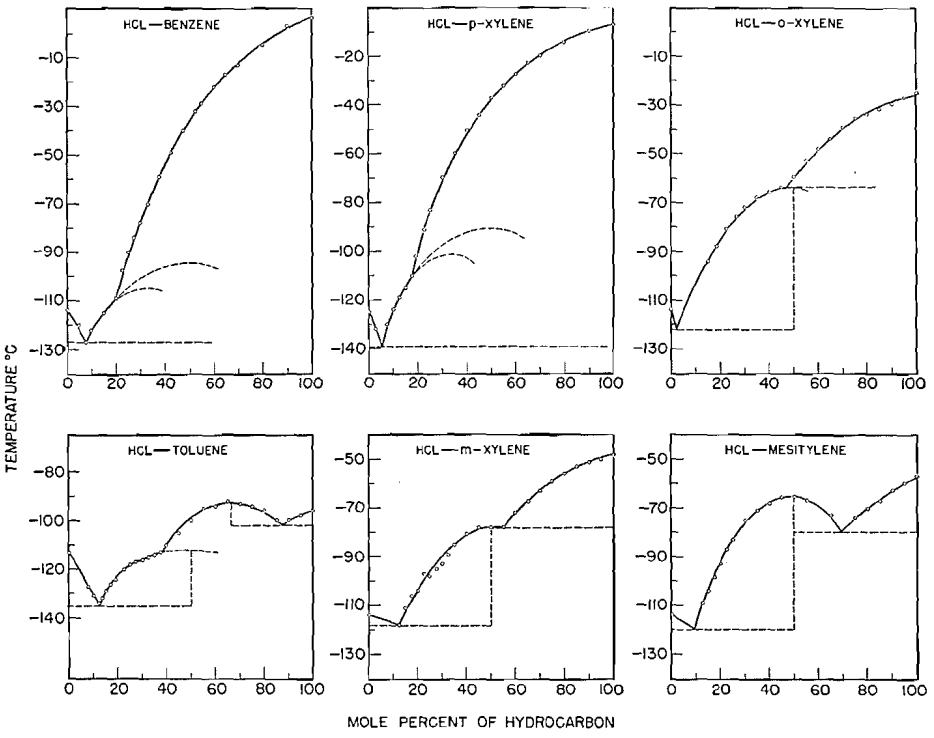

FIG. 1.

TABLE I

SUMMARY OF HYDROGEN CHLORIDE COMPLEXES

Hydrocarbon	Compound, HCl:hydrocarbon	Melting point* (°C.)	Color of complex
Benzene	1:1	−110 (*i*)	Colorless
Toluene	1:1	−112 (*i*)	"
	1:2	− 91	
o-Xylene	1:1	− 64	"
m-Xylene	1:1	− 78	"
p-Xylene	1:1	− 93 (*i*)	"
Mesitylene	1:1	− 66	"
trans-Stilbene	(1:1)		Blue
Anthracene	(1:1)		Yellow

*(*i*)—*Incongruent melting point.*

The phase diagrams of two cyclic saturated hydrocarbons, cyclopropane and cyclohexane, with hydrogen chloride were also determined (Figs. 2*a* and 2*b*). The HCl–cyclohexane system exhibits neither an addition compound nor a eutectic. In this respect the diagram is similar to that of the ethane–HCl and propane–HCl systems. The corresponding diagram for the cyclopropane–HCl system shows only a eutectic point.

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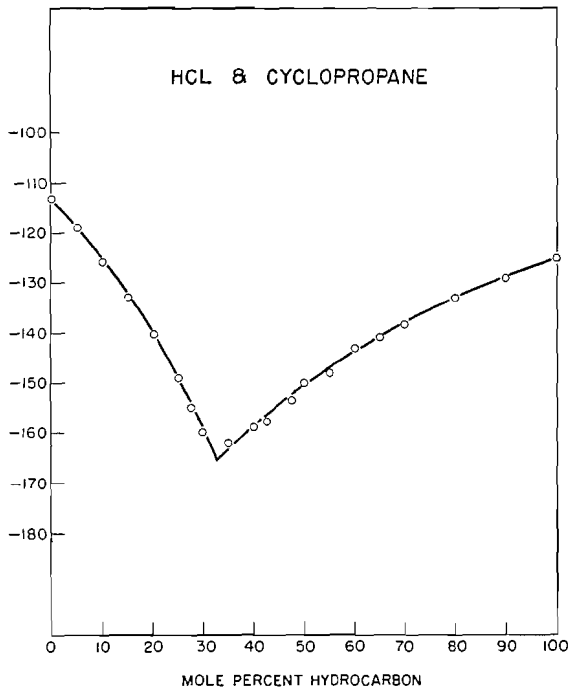

FIG. 2*a*.

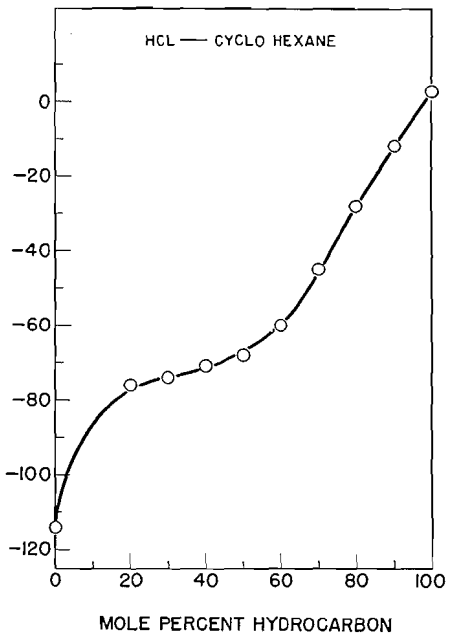

FIG. 2*b*.

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DISCUSSION OF RESULTS

In contrast to the HCl complexes of the olefins and acetylenic hydrocarbons which give rise to several complexes differing in their HCl content, the benzene hydrocarbons form mainly only a 1:1 complex. Toluene, which also gives rise to a 1:2 complex, appears to be an exception to this behavior. Since the saturated cyclic hydrocarbons cyclohexane and cyclopropane do not undergo complex formation with HCl, it must be concluded that, as in the case of the alkenes and alkynes, specific forces of interaction exist between the π-orbitals of the aromatic molecules functioning as donors and the acceptor hydrogen chloride. Since the π-orbitals of the aromatic molecules are much more delocalized than those of the alkene or alkyne molecules, their basic strength may be somewhat weaker and this may contribute to the fact that 1:1 HCl complexes predominate in the former. However this cannot be a complete explanation as other factors, such as the greater polarizability of the aromatic π-orbitals, undoubtedly play a part.

In the complex it appears reasonable to assume that the HCl molecule is oriented with its molecular axis approximately at right angles to the plane of the aromatic molecule and with the hydrogen end directed toward a π-orbital, i.e. toward a carbon atom or a carbon–carbon bond. A further question of interest is whether or not the 1:1 complex exists in the form of discreet dimers, i.e. HCl plus hydrocarbon, which was assumed to be the case for the alkene and alkyne complexes, or whether it forms a repeating chain-like structure.* The latter may be expected to occur if the Cl atom of HCl is capable of interacting with the π-orbitals of a second hydrocarbon molecule, permitting the structure to repeat itself. It is known, for example, that the halogen atoms of alkyl halides interact appreciably with π-orbitals (5) as do also the halogen molecules chlorine, bromine, and iodine.

The anomalous 1:2 HCl–toluene complex is apparently not of the above type. A possible structure, which could account for the observed molecular ratio, is one in which the toluene molecules occur in pairs with their molecular planes parallel and the methyl groups at opposite ends to minimize their mutual repulsion. The pairs could then form a 1:1 complex with HCl. Such a structure, which is entirely speculative, could conceivably be dictated by economy of crystal packing. It is of interest to note that the hydrogen bromide – ethyl benzene system, which was investigated by Maass and Russell (4), also exhibits both a 1:1 and 1:2 compound. These authors also observed a 1:2 compound in the HBr–toluene system but not a 1:1 compound. However, the freezing-point diagrams for the HBr–benzene and HBr–mesitylene systems closely parallel the present results with hydrogen chloride.

The general nature of the freezing-point diagrams indicates the HCl–mesitylene complex to be the most stable and that of ortho- and meta-xylene to be more stable than the complexes of toluene or benzene. Although this is an extremely rough correlation it is also the order of basicity (donor strength)

**It now appears likely that the complexes of chlorine, bromine, or iodine with benzene or the methyl benzenes form chain structures in which the halogen molecule and the hydrocarbon alternate, the axis of the halogen being at right angles to the planes of the hydrocarbon (see J. Collin and L. d'Or. J. Chem. Phys. 23: 397. 1955).*

of these hydrocarbons established by studies of the corresponding iodine complexes (1) and indicated by their relative ionization potentials. A similar correlation of basic strengths has also been reported by Brown and Brady (2). These authors determined the relative solubility of hydrogen chloride in dilute solutions of aromatic hydrocarbons in toluene and in *n*-heptane. Increasing solubility of hydrogen chloride in the dilute solutions was observed in the order: benzene < toluene < *m*-xylene < mesitylene. The solubility results were explained on the basis of π-complex formation of the hydrogen chloride with the π-electrons of the aromatic hydrocarbons.

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THE HYDROLYSIS OF THE CONDENSED PHOSPHATES

III. SODIUM TETRAMETAPHOSPHATE AND SODIUM TETRAPHOSPHATE[1]

By Joan Crowther and A. E. R. Westman

ABSTRACT

The rates of hydrolysis of sodium tetrametaphosphate and tetraphosphate* (in the presence of tetrametaphosphate) have been measured at 65.5°C. over the pH range 2.5 to 13.3. Tetrametaphosphate anions hydrolyze to tetraphosphate which in turn hydrolyzes to triphosphate* and orthophosphate and not to pyrophosphate. Thus the terminal oxygen bridges in the tetraphosphate and not the central one are attacked preferentially. The reactions were first order and acid catalyzed. The tetrametaphosphate hydrolysis was also base catalyzed with a minimum rate in solutions of pH approximately 7.5. The rate of hydrolysis of tetraphosphate was greater than triphosphate at the hydrogen ion concentrations studied. Hydrolysis of a sodium phosphate glass indicated that preferential attack on terminal oxygen bridges takes place also with higher polymers. However, trimetaphosphate is formed at the same time.

INTRODUCTION

Although it is known that both the cyclic polymer tetrametaphosphate and the linear polymer tetraphosphate hydrolyze to form orthophosphate as a final product, little information has been published about their rates or reaction equations. The hydrolysis of tetraphosphate is particularly interesting since this is the lowest in the series of linear phosphates which has more than one mode of attack by a water molecule. If only the middle oxygen bridge is attacked, two moles of pyrophosphate are formed initially; if only an end bridge is attacked, one mole each of triphosphate and orthophosphate are produced; while uniform attack on all oxygen bridges would produce tri-, pyro-, and ortho-phosphate in equimolar amounts. Thus, a study of the hydrolysis of tetraphosphate should increase our knowledge of the properties of phosphate polymers.

The published work on the hydrolysis of tetra- and tetrameta-phosphate is limited and generally inconclusive. Bell, Audrieth, and Hill (1) have examined the hydrolysis of tetrametaphosphate. Their results agree qualitatively with those published in this paper if it is assumed that their analytical procedure was not suitable for determining small quantities of tetraphosphate. By measuring tri-, pyro-, and ortho-phosphate, Rodionova and Khodakov (6) decided that tetrametaphosphate hydrolyzes to tetraphosphate which subsequently hydrolyzes to tri- and ortho-phosphate; the value of their conclusion, however, was limited by their inability to analyze for the compounds with four phosphorus atoms. Such (7) also found evidence by measuring orthophosphate that tetrametaphosphate formed tri- and ortho-phosphate on hydrolysis. On the other hand, Thilo (8) believed that tetraphosphate partially

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Contribution from the Department of Chemistry, Ontario Research Foundation, Toronto 5, Ontario. Presented at the Annual Conference, The Chemical Institute of Canada, June, 1955.
**More specific names in terms of current commercial practice would be hexasodium tetrapolyphosphate and pentasodium tripolyphosphate for sodium tetraphosphate and sodium triphosphate respectively.*

hydrolyzed to form pyrophosphate. Also, Quimby (5) gives four pieces of evidence that "suggest that alkaline media tend to split the tetraphosphate ion into two pyrophosphate fractions" and one piece of evidence which favored end-group cleavage. The latter he attributed to the high temperature reached (92°C.).

In general, evidence based on crystallization or precipitation techniques applied to a solution of hydrolyzates is suspect, since the compound appearing in a primary phase is frequently not the major solute or may even not be present in the solution, particularly when only a small yield is obtained.

Thus the difficulties involved in the analyses have prevented workers from establishing the equations for these hydrolysis reactions, and no quantitative information is available about their rate constants.

In the present work, the analytical problem has not been completely solved,* but the chromatographic procedure (2) employed did permit the determination of all components with a precision of two to three per cent. It has been possible therefore to propose equations for the hydrolysis reactions and to estimate their first-order rate constants at specified hydrogen ion concentrations.

EXPERIMENTAL

Materials

Pure sodium tetrametaphosphate tetrahydrate, $(NaPO_3)_4.4H_2O$, supplied by Albright and Wilson Limited was used. No other phosphates were found in the material (2) and the phosphorus content corresponded to the above formula. The solution used in the experiments contained 0.242 at. wt. of phosphorus per liter—this concentration being suitable for analysis.

Pure tetraphosphate was unobtainable in sufficiently large quantities when this work was in progress and thus a phosphate mixture, in which tetraphosphate was the major component, was used. This mixture was obtained by heating sodium tetrametaphosphate $[(NaPO_3)_4.4H_2O]$, in sufficient normal sodium hydroxide to break the ring, for one hour at 65.5°C. The resultant solution was a mixture of tetra- and tetrameta- with small amounts of tri- and ortho-phosphate anions. After suitable dilution (0.17 at. wt. of phosphorus per liter) this solution was used as the starting material for the hydrolysis study of sodium tetraphosphate.

Procedure

Samples (50 ml.) of the phosphate solutions were adjusted to within 0.1 unit of the desired pH value by adding sodium hydroxide and/or hydrochloric acid solutions of concentration such that a few drops only were required. Since any residual sodium hydroxide would be neutralized in adjusting the pH to the lower values with hydrochloric acid, the solutions might be as much as 0.04 molar in sodium chloride. The solutions were then placed in a long narrow tube and heated in a water bath at 65.5 ± 0.1°C. This temperature was selected

**This and subsequent remarks refer to the period (1954) during which most of this work was done. With techniques and materials now available (1956) errors can be kept within one per cent. A. E. R. W.*

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so that results could be compared with previous work (3). The starting time was initially assumed to be the time at which the solutions were placed in the bath. Since both reactions studied were first order, zero time was later checked by plotting $\log(a_0-a)$ against time. No adjustments were required. The pH value of the solutions was then adjusted to the desired value and maintained within ± 0.1 unit (unless otherwise specified in the following text) by the addition of drops of hydrochloric acid and/or sodium hydroxide solutions. (The concentrations of these solutions varied from normal to tenth normal depending on the sensitivity of the pH range.) The pH values were measured with a glass electrode and a Leeds and Northrup pH meter. At measured time intervals, samples were withdrawn and spotted on filter-paper chromatograms within one minute. Further hydrolysis during the analysis was negligible.

In the hydrolysis studies at pH 9.8, the pH of the solutions was not controlled as accurately as indicated above. During the day, the solutions were maintained at 9.8 ± 0.1 pH but during the night the pH fell from 10.2 to values as low as 9.0. Although this situation was undesirable, the rates of hydrolysis of tetrameta- and tetra- are comparatively insensitive to pH in this region (Fig. 4). Lastly, no pH control was attempted for the study of the hydrolysis of tetrametaphosphate at pH 13 owing to the insensitivity of the pH meter in this range. Thus the pH of this solution decreased from 13.4 to 12.7 during the course of the experiment, and the results are tabulated (Table I) for the average value 13.

Analysis

The analyses were carried out using a procedure developed in these laboratories (2). The method involves the separation of the phosphate components by filter-paper chromatography followed by a colorimetric determination of the amount of phosphorus in each component.

The analytical procedure had a serious drawback. Although the five components could be separated by filter-paper chromatography, the chromatographic techniques were such that it could not be efficiently done every time. Since the samples change on standing, there was no opportunity to repeat an analysis. Thus the precision of the analyses varied from one to three per cent. This defect is most apparent in the study of the hydrolysis of tetrametaphosphate anions. Here the normal mixture had a large proportion of tetrametaphosphate and small amounts of the other components—the most difficult type of chromatographic separation. In one set of analyses (pH 2.50) the resolution on the chromatograms of pyro- and tri-phosphate was so poor that only their sum is quoted. Consequently, the rate constants for this pH are approximate only. Although the analyses were not as precise as desired, yet they can be considered reliable in another sense since most of them were checked by different chromatographic procedures.

Data

The hydrolysis of sodium tetrametaphosphate in solution was studied at 65.5 ± 0.1°C. at pH values of 2.50, 5.30, 9.8, and approximately 13 (initial 13.4, final 12.7). The solution concentration was 0.242 at. wt. of phosphorus

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TABLE I

HYDROLYSIS OF TETRAMETAPHOSPHATE

pH	Reaction time, min.	Distribution of phosphorus (%) Tetra-meta-	Tetra-	Tri-†	Pyro-	Ortho-	First order rate constant (k) of tetrameta-, min.$^{-1}$	Average k, min.$^{-1}$
2.50	0	100	0	0*		0		
	1223	90.8	0.5	4.3*		4.4	7.9×10^{-5}	
	1485	89.4	0	6.6*		4.0	7.5 "	
	2645	87.8	1.9	5.3*		5.0	4.9 "	
	2922	82.8	2.1	7.3*		7.8	6.4 "	
	3925	69.7	4.9	12.3*		13.1	9.2 "	
	4085	68.4	3.7	10.4*		17.5	9.3 "	
	5742	61.2	6.4	16.9*		15.5	8.5 "	7.7×10^{-5}
5.30	0	100	0	0	0	0		
	1355	94.9	0	5.1	0	0	Negligible	
	1840	100.4	0	−0.4	0	0	"	
	2795	101.5	0	−1.5	0	0	"	
	2910	101.5	0	−1.5	0	0	"	
	3240	101.0	0	−1.0	0	0	"	
	4235	97.1	0	2.9	0	0	"	
	4325	102.6	0	−2.6	0	0	"	
	4712	100.3	0	−0.3	0	0	"	
	5840	95.0	0	5.0	0	0	"	
	6141	100.0	0	0	0	0	"	Negligible
9.8	0	100	0	1.4	0	0		
	1383	99.3	0	0.7	0	0	5.3×10^{-6}	
	1500	97.8	0	2.2	0	0	15.0 "	
	1760	97.8	0	2.2	0	0	13.0 "	
	3228	98.1	0	1.9	0	0	5.9 "	
	4253	96.9	0	3.1	0	0	7.5 "	
	4680	96.0	0	4.0	0	0	8.7 "	
	5697	96.9	0	3.1	0	0	5.6 "	
	6114	97.2	0	2.8	0	0	4.7 "	8×10^{-6}
13.0	0	100	0	0	0	0		
	30	100.3	0	−0.3	0	0	Negative	
	60	99.5	0	0.5	0	0	0.9×10^{-4}	
	120	97.3	0.5	2.2	0	0	2.3 "	
	180	94.5	4.4	1.1	0	0	3.1 "	
	210	97.8	1.2	1.0	0	0	1.1 "	
	241	95.9	3.2	0.9	0	0	1.7 "	
	270	93.8	6.5	−0.3	0	0	2.4 "	1.9×10^{-4}

**The sum of per cent phosphorus found in form of pyro- and tri-phosphate.*

†In chromatograms for Table I, some tetrameta- trailed back to the tri- position. The analyses were calculated on the assumption that this was consistent. This accounts for the uncertainty in the tri- percentages reports. Techniques developed later eliminated this difficulty and were used for the analyses reported in Table II.

per liter. The phosphorus distributions of the solutions at various times are given in Table I.

The hydrolysis of sodium tetraphosphate – sodium tetrametaphosphate mixtures in solution was studied at 65.5±0.1°C. at pH values of 2.55, 5.35, 9.8, and 13.3. The solutions' concentration was 0.17 at. wt. of phosphorus per liter. The compositions of the solutions after various time intervals are given in Table II and are plotted in Figs. 1, 2, and 3 for pH values of 5.35, 9.8, and 13.3 respectively. In every case the values for zero time are based on four to eight separate analyses.

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TABLE II

HYDROLYSIS OF TETRAPHOSPHATE

pH	Reaction time, min.	Distribution of phosphorus (%)					First order rate constant (k) of tetra-, min.$^{-1}$	Average k, min.$^{-1}$
		Tetra-meta-	Tetra-	Tri-	Pyro-	Ortho-		
2.55	0	32.4	62.4	3.8	0	1.3		
	120	32.9	50.6	9.1	1.7	5.7	1.8×10^{-3}	
	240	32.2	45.0	12.4	4.0	6.4	1.4×10^{-3}	
	300	32.4	34.3	19.5	5.3	8.5	2.0×10^{-3}	
	360	33.3	30.2	24.2	2.4	9.8	2.0×10^{-3}	1.8×10^{-3}
5.35	0	39.1	57.7	3.2	0	0		
	398	37.4	41.9	12.7	0	8.1	$8.1^{*}\times10^{-4}$	
	1349	36.2	18.6	20.2	5.8	19.3	$8.4^{*}\times10^{-4}$	
	1838	35.8	12.3	17.9	7.4	26.6	$8.4^{*}\times10^{-4}$	
	2792	37.8	7.1	15.2	12.0	27.9	7.5×10^{-4}	
	3260	38.5	6.7	12.0	14.2	28.6	7.6×10^{-4}	
	4238	37.4	4.1	9.9	14.8	33.9	6.2×10^{-4}	
	4560	36.8	2.6	9.1	14.8	36.7	6.8×10^{-4}	
	4690	38.9	3.2	8.9	13.9	35.1	6.2×10^{-4}	
	5685	39.7	2.4	6.2	13.9	37.8	5.6×10^{-4}	8.3×10^{-4}
9.8	0	22.6	63.3	9.0	0	5.1		
	298	19.3	58.5	12.5	0	9.7	2.1×10^{-4}	
	1252	24.2	45.4	20.8	1.8	7.8	2.7×10^{-4}	
	1452	25.2	42.0	22.0	1.6	9.2	2.8×10^{-4}	
	1585	22.8	42.6	23.4	2.3	8.9	2.5×10^{-4}	
	1715	23.2	41.3	21.6	2.2	11.7	2.5×10^{-4}	
	2705	24.4	32.9	29.4	4.1	9.2	2.4×10^{-4}	
	2880	25.1	27.4	29.2	4.4	13.9	2.9×10^{-4}	
	3150	22.7	32.5	28.0	2.6	14.2	2.1×10^{-4}	
	4140	22.3	22.7	35.3	3.2	16.5	2.5×10^{-4}	
	4329	20.6	25.2	34.8	3.7	15.8	2.1×10^{-4}	2.5×10^{-4}
13.3	0	34.0	60.7	4.6	0	0.8		
	155	27.2	60.0	9.8	0	3.0		
	410	15.9	68.8	9.2	1.9	4.2		
	1368	4.1	68.2	18.6	1.6	7.6		
	1850	3.2	55.5	30.0	2.0	9.3		
	2809	0	45.9	34.1	3.6	16.4		
	2990	0	44.4	37.0	2.4	16.2		
	3295	0	44.1	37.0	2.6	16.2		
	4246	0	34.9	36.8	5.6	22.7		
	4721	0	36.5	38.9	4.4	20.2		
	5683	0	16.0	55.5	5.5	23.0		
	5905	0	16.5	55.8	5.1	22.5		
	6145	0	22.3	50.0	5.9	21.8		2.5×10^{-4}†

**Only these figures were used to calculate the first order rate constant.*
†For tetrametaphosphate 1.8×10^{-3} min.$^{-1}$.

Calculations

(*a*) *Tetrametaphosphate Data from Table I*

When the data for the hydrolysis of tetrametaphosphate anions (Table I) were substituted in the general equation for a first-order reaction, the rate constants 8×10^{-5}, 6×10^{-6}, and 2×10^{-4} min.$^{-1}$ were obtained for solutions with pH values of 2.50, 9.8, and approximately 13, respectively. The degree of hydrolysis at pH 5.30 was negligible even after 100 hr., while at pH 9.8 it was so small ($k = 6\times10^{-6}$ min.$^{-1}$) that the apparent hydrolysis could be due to experimental error. The values of the rate constants for each time interval

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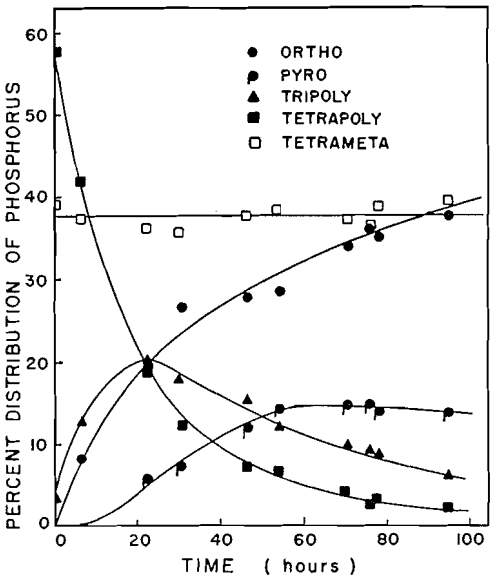

FIG. 1. Progress of hydrolysis, pH = 5.35.

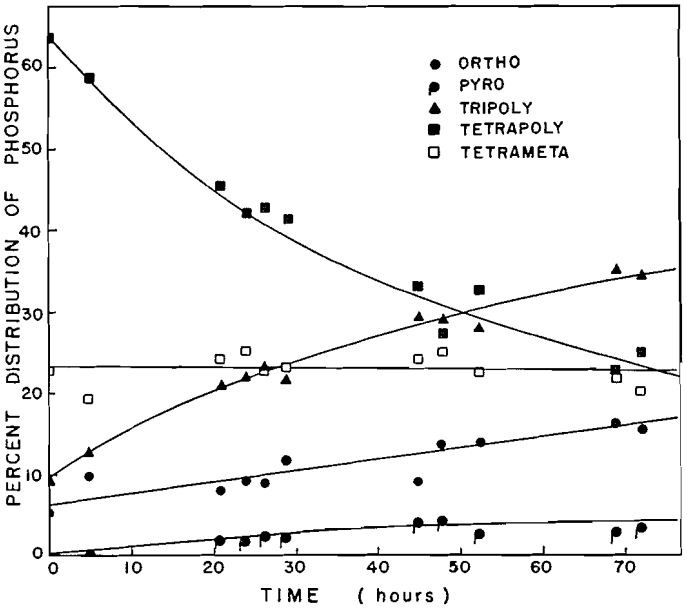

FIG. 2. Progress of hydrolysis, pH = 9.8.

measured from zero time are given in Table I along with the average values for each hydrogen ion concentration studied. The latter are plotted in Fig. 4 along with one value from Table II (pH 13.3) and with corresponding values for tri- and pyro-phosphate from Paper I (3) of this series. Within the limitations of the analytical methods, the data of Table I fit the equation for a first-order reaction, but more precise data might reveal departures from this.

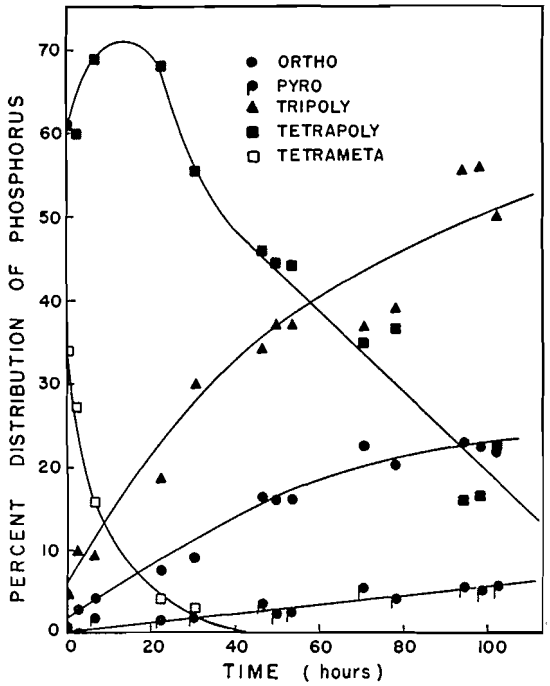

FIG. 3. Progress of hydrolysis, pH = 13.3.

(*b*) *Tetraphosphate Data from Table II*

The data for the hydrolysis of tetraphosphate anions in Table II fit the general equation for a first-order reaction for solutions with pH values of 2.55, 5.35, and 9.8. The values obtained for these first-order rate constants are included in Table II and plotted in Fig. 4. The standard first-order rate equation was used in these calculations since the rate of hydrolysis of tetrametaphosphate anions was so slow over this pH range that no effects from its decomposition were discernible; at pH 2.55 the experiment was limited to six hours to ensure this situation. These calculations, however, assume that the rate of hydrolysis of tetraphosphate is not affected by the presence of tetrametaphosphate.

At pH 13.3 the effects of the decomposition of tetrametaphosphate are evident, and the rate constants for both tetrametaphosphate and tetraphosphate anions were obtained from the equation (solved by approximation)

$$be^{k_1 t} = k_1 a_0 (1 - e^{-(k_2 - k_1) t}) / (k_2 - k_1) + b_0 e^{-(k_2 - k_1) t}$$

where a = fraction of total phosphorus atoms present in the form of tetrametaphosphate at time t,

b = fraction of total phosphorus atoms present in the form of tetraphosphate at time t,

a_0 = value of a at $t = 0$,

b_0 = value of b at $t = 0$,

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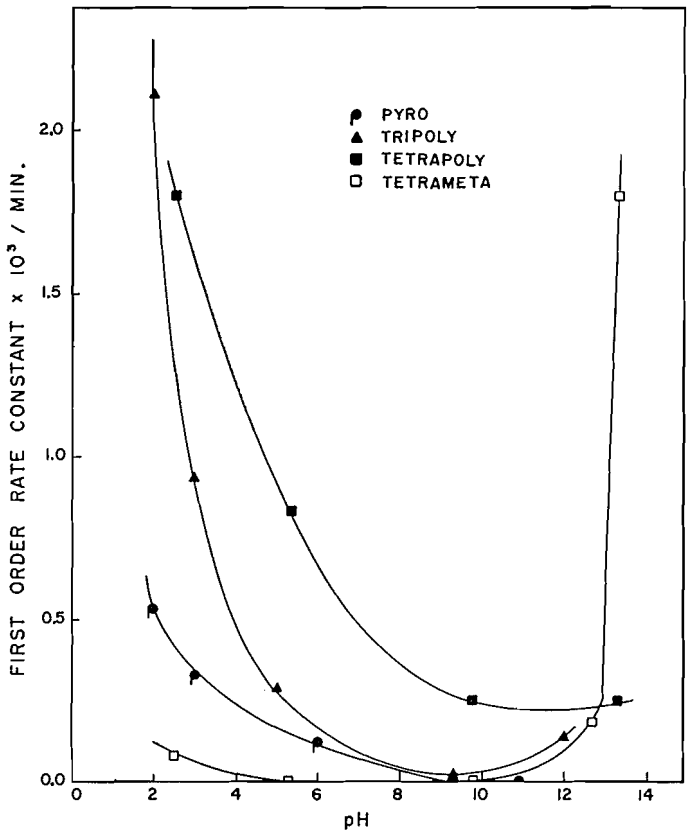

FIG. 4. Effect of pH on rates of hydrolysis of sodium phosphates.

k_1 = first-order rate constant for the hydrolysis of tetrametaphosphate anions,

k_2 = first-order rate constant for the hydrolysis of tetraphosphate anions.

This equation assumes that tetrametaphosphate hydrolyzes to tetraphosphate which in turn hydrolyzes, that both reactions are first order, and that these phosphates hydrolyze independently of each other. The justification of the first assumption is discussed in the following section. The values obtained for the rate constants were 1.8×10^{-3} min.$^{-1}$ and 2.5×10^{-4} min.$^{-1}$ for tetrameta- and tetra-phosphates respectively. This value for tetrametaphosphate is about 10 times that given for pH 13 in Table I. This is due to the fact that the rate of hydrolysis of tetrametaphosphate rises very abruptly in the neighborhood of pH 13 which is probably connected with the rapid rise in the concentration of sodium hydroxide required to reach pH values above pH 13.

When the pH of the solution is 5.35, the data for the hydrolysis of tetraphosphate anions do not fit the first-order equation after 85% of the tetraphosphate phosphorus is no longer in tetraphosphate form suggesting that deviations from first-order behavior may generally be expected in the final stages of this reaction.

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DISCUSSION

(*a*) *Effect of pH*

The rate of hydrolysis of tetrametaphosphate anions (Table I and Fig. 4) is practically negligible over the range pH 5 to 10 but it increases at both ends of the scale.

The rate of hydrolysis of tetraphosphate anions, on the other hand, is effectively catalyzed by acid, but no increase in rate was observed over the pH range 7 to 13.3. This is surprising since tetraphosphate resembles chemically triphosphate and the latter shows such an increase (3), which Van Wazer has found to be a sodium ion effect (10). It is possible, of course, that the hydrolysis of tetraphosphate would show an acceleration if the alkalinity of the solution were further increased.

The great difference in rate between tetrameta- and tetra- in the region of pH 13.3 suggested a method for preparing solutions high in sodium tetraphosphate by hydrolysis of tetrameta-, which was readily available. When such a solution was converted to the ammonium form by ion exchange, concentrated (but not too far!) under vacuum, and allowed to stand at room temperature, plentiful crystals of ammonium tetraphosphate were obtained by P. A. Gartaganis in these laboratories. However, it was found that this work had been largely anticipated by Quimby (5), who prepared the more stable hexaguanidinium tetraphosphate.

In addition, the lead and barium tetraphosphates have been crystallized from melts by Langguth, Osterheld, and Karl-Kroupa (4). Thus, the earlier chromatographic evidence for the tetraphosphate ion (11) has been amply confirmed.

(*b*) *Reactions*

(*i*) *Tetrametaphosphate Hydrolysis*

At least some of the tetrametaphosphate must hydrolyze to tetraphosphate, since the latter is found whenever the rate of hydrolysis of tetrametaphosphate is appreciable (Table I, pH 2.5 and approximately 13). Over most of the pH range studied, the tetraphosphate hydrolyzed at a comparatively rapid rate (Table I vs. II and Fig. 4). Consequently, it cannot be established by inspection of the data that all tetrametaphosphate hydrolyzed to tetraphosphate, although there is a definite indication in the case of pH 13, Table I, where rate relations are more favorable.

In what follows, it is assumed that the tetrametaphosphate hydrolyzed first to tetraphosphate, i.e. the ring was not broken at two, three, or four oxygen bridges simultaneously to produce tri-, pyro-, or ortho-phosphate directly from the tetrametaphosphate. The best demonstration of this proposed reaction is given in Table II (data for pH 13.3) and Fig. 3. At this pH value, the rate of hydrolysis of tetraphosphate anions is less than that for tetrametaphosphate anions, and the proportion of phosphorus as tetraphosphate increases in the initial stages of the experiment owing to the hydrolysis of the cyclic phosphate.

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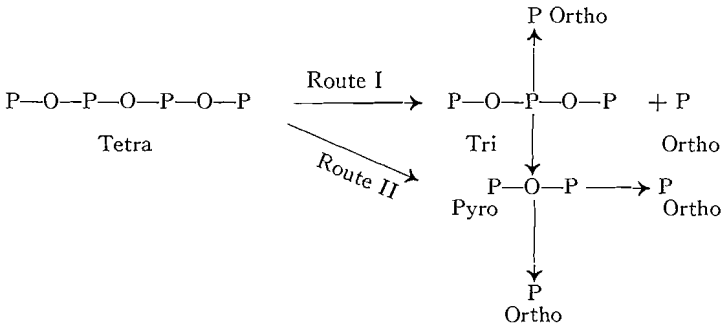
(ii) Tetraphosphate Hydrolysis

As indicated earlier, the hydrolysis of tetraphosphate might proceed by two routes designated I and II in the following diagram where the phosphorus–oxygen skeletons are used to represent the ions concerned.



Route I involves attack on one end phosphorus–oxygen bridge exclusively; Route II on only the middle oxygen bridge. Inspection of Tables I and II and Figs. 1, 2, and 3 shows many cases in which the triphosphate content increases in unmistakable fashion to an extent that shows that Route I is at least the predominant route. In some cases, however, this effect is obscured to some extent by the rapid hydrolysis of the triphosphate and there is also the question as to whether one can say, within the limitations of the analytical method, that there is no direct hydrolysis to pyrophosphate, i.e. no attack on the middle oxygen bridge.

One method of examining this question by purely stoichiometric calculation, except for a small correction for initial tri- and pyro-, is illustrated in Table III. In this table, the data of Table II are corrected for the effect of the initial tri-, pyro-, and ortho- using the rate constants derived previously. The net increase in tri- at any time is multiplied by four-thirds to determine the minimum amount of phosphorus that has certainly gone by Route I according to the analysis. This is calculated as a percentage of the net phosphorus lost by (tetrameta- + tetra-) and reported in Column 7. The remainder of the phosphorus lost by (tetrameta- + tetra-) is then assigned to pyro- and ortho- by assuming Route I (Columns 8, 9), Route II (Columns 9, 10), and a negligible rate of pyro- hydrolysis. These calculated values may be compared with the corresponding observed values (Columns 6, 7).

At pH 9.8, the minimum percentage by Route I averages 86% and the remainder is distributed between pyro- and ortho- as expected if Route I is followed. Since the hydrolysis rate for pyro- at pH 9.8 is very slow, it may be concluded that the data do not lend any support to the hypothesis that any phosphorus follows Route II.

At pH 13.3, the minimum percentage by Route I averages 90%. The distribution of the remainder is not conclusive since it might have been obtained via Route I or II although the latter would require more hydrolysis of pyro-. There is an indication here that possibly pyro- is slightly base catalyzed.

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TABLE III

STOICHIOMETRIC TEST FOR REACTION ROUTE

pH	Reaction time, min.	Analysis corrected for effect of initial tri-, pyro-, and ortho-					Minimum percentage by Route I, %	Distribution of remainder					
								Observed		Calculated by Route I		Calculated by Route II	
		Tetra-meta-	Tetra-	Tri-	Pyro-	Ortho-		Pyro-	Ortho-	Pyro-	Ortho-	Pyro-	Ortho-
2.55	0	34.2	65.8	0	0	0							
	120	34.7	53.4	6.0	1.5	4.5	66.6	1.48	2.53	2.60	1.30	3.90	0
	240	34.0	47.4	10.0	3.7	5.1	74.8	3.69	1.69	3.45	1.72	5.17	0
	300	34.2	36.2	17.5	5.0	7.3	79.0	4.96	1.37	4.15	2.08	6.23	0
	360	35.1	31.8	22.7	1.8	8.5	91.4	1.79	1.06	1.90	0.95	2.85	0
	Av.						77.0						
5.35	0	40.4	59.6	0	0	0	—						
	398	38.6	43.3	10.1	−0.2	8.3	74.9	−0.21	5.9	3.03	1.52	4.55	0
	1349	37.4	19.2	18.5	5.4	19.5	56.9	5.48	13.3	12.5	6.2	18.7	0
	1838	37.0	12.7	16.4	6.9	27.0	24.4	6.92	21.7	18.9	9.5	28.4	0
	2792	39.0	7.3	14.1	11.6	28.0	34.0	11.6	23.9	23.6	11.8	35.4	0
	3260	39.8	6.9	11.0	13.7	28.6	27.5	13.7	24.9	25.8	12.8	38.6	0
	4238	38.6	4.2	9.1	14.3	33.8	21.4	14.3	30.7	30.0	15.0	45.0	0
	4560	38.0	2.8	8.5	14.3	36.7	20.0	14.3	33.2	31.7	15.8	47.5	0
	4690	40.2	3.3	8.2	13.3	35.0	19.2	13.3	32.4	30.4	15.2	45.6	0
	5685	41.0	2.5	5.6	13.3	37.5	13.2	13.3	35.6	32.7	16.3	49.0	0
	Av.						32.4						
9.8	0	26.4	73.7	0	0	0							
	298	22.5	68.2	4.1	0	5.4	57.7	0	4.00	2.66	1.33	4.00	0
	1252	28.2	52.9	14.0	1.9	3.1	98.2	1.86	−1.52	0.23	0.12	0.35	0
	1452	29.4	49.0	15.4	1.6	4.8	94.2	1.63	−0.35	0.85	0.43	1.28	0
	1585	26.6	48.6	17.0	2.4	4.4	94.4	2.44	−1.12	0.88	0.44	1.33	0
	1715	27.0	48.1	14.9	2.3	7.7	79.7	2.33	2.72	3.36	1.68	5.05	0
	2705	28.4	38.4	24.2	4.3	4.8	97.0	4.31	−3.26	0.70	0.35	1.05	0
	2880	29.2	31.9	24.0	4.7	10.3	82.0	4.66	2.33	4.65	2.37	6.98	0
	3150	26.4	37.9	22.6	2.6	10.6	84.3	2.56	3.09	3.76	1.88	5.65	0
	4140	26.0	26.4	31.2	3.0	13.3	87.3	3.03	2.91	4.03	2.01	6.05	0
	4329	24.0	29.4	30.8	3.6	12.5	87.8	3.61	2.21	3.80	1.90	5.70	0
	Av.						86.3						
13.3	0	36.0	64.1	0	0	0	—						
	155	28.6	63.5	5.6	−0.1	2.3	95.5	−0.11	0.45	0.23	0.12	0.35	0
	410	16.8	72.8	5.2	1.8	3.5	66.0	1.80	1.76	2.37	1.19	3.56	0
	1368	4.3	72.0	15.8	1.1	6.9	89.2	1.06	1.58	1.69	0.85	2.54	0
	1565	0.3	61.9	24.6	1.2	7.2	100.0	1.16	−1.06	0	0	0	0
	1850	3.4	59.6	28.1	1.3	8.6	98.6	1.27	−0.74	0.35	0.18	0.53	0
	2809	0	48.5	33.0	2.6	15.9	85.5	2.64	4.86	5.00	2.51	7.51	0
	2990	0	47.0	36.0	1.3	15.6	70.7	1.27	3.6	3.31	1.65	4.96	0
	3295	0	46.6	36.2	1.5	15.6	90.5	1.48	3.6	3.38	1.69	5.07	0
	4246	0	36.9	36.4	4.3	22.3	77.0	4.34	10.15	9.66	4.84	14.5	0
	4721	0	38.6	38.8	3.0	19.7	84.3	2.96	6.66	6.40	3.21	9.61	0
	5683	0	16.9	56.7	3.9	22.4	91.0	3.91	3.49	5.00	2.50	7.50	0
	5905	0	17.4	57.0	3.5	21.9	92.3	2.49	2.86	4.30	2.15	6.45	0
	6145	0	23.6	51.0	4.2	21.2	89.3	4.23	4.01	5.50	2.75	8.25	0
	Av.						89.5						

At pH 5.35 the triphosphate and pyrophosphate are breaking down rapidly enough so that a purely stoichiometric test is not so conclusive. However, it will be observed that the triphosphate builds up before the pyrophosphate.

At pH 2.55 the reaction was not carried to the point where the triphosphate content starts to decrease. At least, triphosphate is the initial product.

Within the limitations of the analytical methods, therefore, it may be concluded that the hydrolysis of tetraphosphate occurs predominantly and quite probably exclusively by attack on an end oxygen–phosphorus bridge.

This may be a general rule for linear polyphosphates. In addition, it may be seen from Fig. 4 that the rate of hydrolysis for tetraphosphate is greater than that for triphosphate which, in turn, is greater than that for pyrophosphate. From this it could be expected that, if a polyphosphate glass having only medium length or longer polymers is used as a starting material in a hydrolysis experiment, the only low molecular weight phosphate formed initially should be orthophosphate and this could readily be determined by chromatographic or even chemical methods. Such an experiment was carried out later by P. A. Gartaganis of these laboratories. The data are given in Table IV. They show a

TABLE IV

HYDROLYSIS OF A PHOSPHATE GLASS
(pH = 3, 65.5°C., initial chain length = 17)

Weight per cent distribution of phosphorus	Time in minutes			
	0	295	625	1440
Ortho-	0.0	5.6	9.6	19.6
Pyro-	3.4	2.7	3.6	5.3
Tri-	7.5	4.5	5.5	6.2
Tetra-*	7.0	8.4	12.4	14.9
Penta-†	8.8	7.0	7.0	6.2
Hexa-	7.1	8.0	7.8	6.2
Hepta-	6.8	6.8	6.1	5.0
Octa-	5.4	6.0	5.2	4.5
Nona-	5.4	6.2	5.5	3.8
Hypoly-	48.6	44.7	37.3	28.2
	100.0	99.8	100.0	99.9

*Plus trimeta-.
†Plus tetrameta-.

pronounced decrease in hypoly-, increase in ortho-, and increase in (tetra- + trimeta-). Chromatographing in other solvents showed that the last was due to a striking increase in trimeta-. Thus, two mechanisms were operating: (*a*) splitting off of end ortho- groups in all categories and (*b*) production of trimeta- from hypoly-. The latter accounts for about one-half the loss of hypoly-. Apparently, it was not accompanied by mid-chain breakage, so that something more detailed than the mechanism postulated by Thilo, Schulz, and Wichmann (9) may be necessary.

(*c*) *Independence*

The question as to whether each of the four condensed phosphates hydrolyzed in these experiments is hydrolyzed at a rate which is not affected by the other

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phosphates present can be examined by means of the data given here. It involves the calculation of a number of chemically consecutive reactions occurring simultaneously and will be the subject of a later paper.

CONCLUSIONS

(*a*) *Order*

Tetrameta-, tetra-, tri-, and pyro-phosphate hydrolyze at constant pH by first-order kinetics for most of the course of the reaction.

(*b*) *Equations*

Tetrameta- hydrolyzes to tetra- which in turn hydrolyzes to tri- and ortho-. No evidence of a direct hydrolysis of tetra- to pyro- was found so that little if any attack occurs at the middle oxygen bridge in a tetraphosphate anion.

(*c*) *Rate Constants*

The rate constant for tetrameta- is very small except at very high pH values in the neighborhood of or above pH 13.

The rate constant for tetra- is greater than those for tri- and pyro- over the pH range studied, but shows no evidence of base catalysis at pH 13.3.

The progression from pyro- to tri- to tetra- is therefore not uniform as far as base catalysis is concerned but tetra- may be base catalyzed at higher alkalinities than those studied.

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THE CONVERSION OF HYODESOXYCHOLIC ACID TO PROGESTERONE[1]

By K. R. Bharucha, G. C. Buckley, C. K. Cross, L. J. Rubin, and P. Ziegler

ABSTRACT

A novel transformation of 3α,6α-dihydroxy steroids to their 3β-hydroxy-Δ[5] analogues was developed and applied to the preparation of progesterone from hyodesoxycholic acid.

Hyodesoxycholic acid was first isolated from hog bile by Windaus (17) who showed it to be a 3,6-dihydroxycholanic acid. The configurations of the two hydroxyl groups however were not elucidated until recently when they were assigned the α-positions (10). Since then this bile acid has not received a great deal of attention despite the fact that it represents a by-product of packing house operations. One of the reasons for this lack of interest has been undoubtedly the difficulty of its isolation from the crude animal bile, and only recently have adequate isolation procedures been worked out (2, 14). As a result, hyodesoxycholic acid is now a readily accessible material and it was the object of our work to utilize this bile acid for the preparation of physiologically active steroids.

Two major changes must be performed in order to convert methyl hyodesoxycholate (I*a*) to progesterone (XII). Firstly the side chain has to be degraded with loss of three carbon atoms and secondly the 3α,6α-dihydroxy grouping has to be transformed to the 3-keto-Δ[4] structure.

The side chain of I has previously been degraded by the classical Barbier–Wieland method to provide 3,6-dihydroxy-pregnan-20-one (7, 9). Later on, the procedure of Meystre and Miescher was applied to the same problem and resulted in greatly improved yields (6, 11). Our experiments were designed to improve this latter procedure, and at the same time the intermediate products were isolated and characterized. One of the modifications developed in the course of this work concerned the reaction of III*b* with N-bromosuccinimide which in the past was carried out in carbon tetrachloride with a light catalyst. This is hazardous on a large scale and also requires the installation of expensive equipment. It was found that a chemical free radical promoter such as diacetyl peroxide or α,α′-azo-diisobutyronitrile could be used instead of the light catalyst. The use of hydrocarbon solvents was found to be much superior to carbon tetrachloride since the brominated product was quite stable in hexane or commercial hydrocarbon mixtures in contrast to the chlorinated solvents. Various other modifications, of a minor nature, are described in the experimental section but it may be pointed out that these have significantly contributed to greatly enhanced yields (55% of VIII*a* from I*a*).

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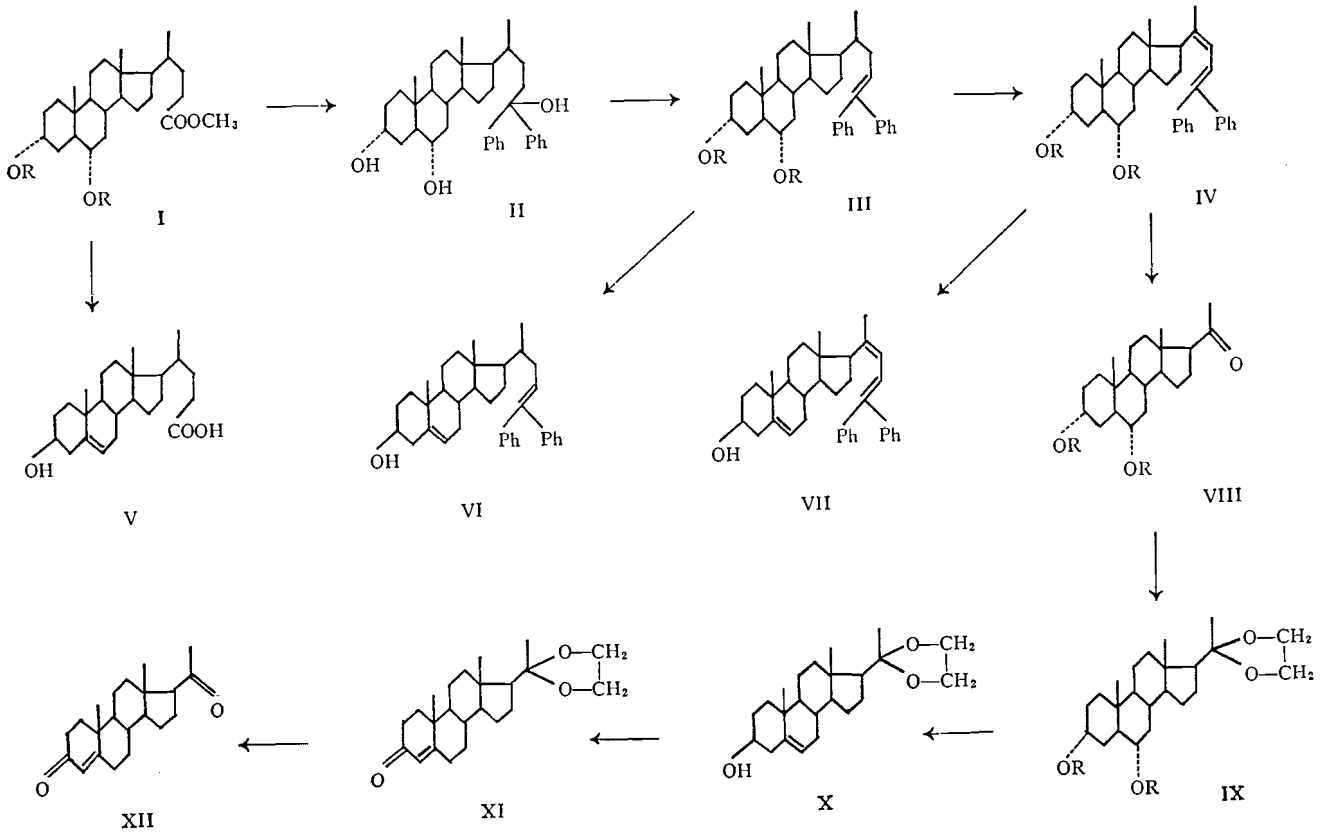

a, R = H *b*, R = Ac *c*, R = CH_3—C$_6$H$_4$—SO_2—

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It then remained to develop a method whereby the 3α,6α-dihydroxy grouping could be converted in good yield to the 3-keto-Δ^4 analogue. The earliest attempts in this direction had been made by Marker (8, 9) who obtained progesterone by preferential hydrolysis of 3α,6α-diacetoxy-pregnan-20-one (VIII*b*) to the corresponding 3α-hydroxy-6α-acetoxy compound, followed by oxidation and dehydration. This was confirmed (4) when a small amount of 3-keto-6α-hydroxycholanic acid was isolated from I*b* by partial hydrolysis and subsequent oxidation. Several investigators then turned their attention to the use of preferential oxidations which would directly give 3-keto-6α-hydroxy steroids which in turn could be dehydrated readily. These oxidations were carried out by using Raney nickel with cyclohexanone (5, 6), aluminum tertiary butoxide and acetone (4), aluminum phenylate and acetone (5, 16), and N-bromosuccinimide in aqueous acetone (12, 13). Without exception the 3-keto-6-hydroxy derivative was accompanied by 3,6-diketo compounds and by unreacted starting material, and in most cases chromatography had to be resorted to in order to isolate the desired product. The 3-keto-6-hydroxy steroid was then transformed to the corresponding 3-keto-Δ^4 analogue by tosylation and dehydrotosylation (4, 5, 6) or by treatment with phosphorus oxychloride in pyridine (12, 13). Yamasaki (18, 19) then discovered that methyl hyodesoxycholate could be dehydrated to 3β-chloro-Δ^5-cholenic acid by the action of phosphorus oxychloride; treatment with potassium acetate, followed by saponification, provided 3β-hydroxy-Δ^5-cholenic acid. Two alternative methods for the preparation of 3β-acetoxy-Δ^5 steroids from the corresponding 3α,6α-ditosylates by treatment with silver acetate in acetic acid (1) or potassium acetate in acetic anhydride (15) have recently been reported. The yields are 30% and 45% respectively.

The approach that was used in our laboratories was similar to the methods referred to above (1, 15). We first tosylated methyl hyodesoxycholate to give quantitatively the corresponding ditosylate (I*c*). When the latter was refluxed with metal acetates in acetic acid it yielded, after saponification, 30% of V. When the dehydrotosylation was carried out in a neutral solvent such as acetic anhydride or aqueous acetone the yield of V increased to 50%. In these reactions there was invariably obtained a large amount of heteroannular dienes as shown by their ultraviolet absorption at 235 mμ. An improved procedure which we reported in an earlier note (20) employed a reaction medium of potassium acetate in aqueous dimethylformamide and in this way a marked increase in yield (70–75%) was achieved. The same results were obtained when N-methyl-pyrrolidone or N,N-dimethylacetamide was used. This method was then applied successfully to the products derived from the side-chain degradation of hyodesoxycholic acid and the desired 3β-hydroxy-Δ^5 steroids were isolated by crystallization. However, when 3α,6α-ditosyloxy-pregnan-20-one (VIII*c*) was treated accordingly the products had to be chromatographed to provide pure pregnenolone and besides the yield was lower than expected. This was due to the alkaline conditions prevailing during the dehydrotosylation reaction which probably cause racemization at C-17 of the steroid nucleus. To overcome this difficulty the keto group in VIII*a* was protected by formation

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of the ethylene ketal IX*a*; the latter was then tosylated and dehydrotosylated in the usual manner, the 20-ketone group being regenerated by mild acid hydrolysis either before or after the Oppenauer oxidation. In this fashion progesterone was obtained from hyodesoxycholic acid in 30–35% yield.

During the dehydrotosylation of 3α,6α-ditosyloxy steroids, having a ring A/B *cis* junction, several reactions take place. There is an S_N2 mechanism operative at C-3 as evidenced by complete inversion at this location—a careful chromatography of the products failed to reveal any traces of the 3α-epimer. The formation of the double bond in ring B is due to an elimination reaction of the E1 type. As stated before there is always obtained a quantity of heteroannular diene which results from elimination both at C-6 and at C-3. It is interesting to observe that as the reaction medium is changed from acetic acid to acetic anhydride to aqueous dimethylformamide, the amount of 3β-hydroxy-Δ^5 steroid increases while the yield of diene decreases. The ratio of these products depends entirely on the relative rates of substitution and elimination. Since the 3α-tosyloxy group in compounds such as *Ic* is equatorial and therefore not inclined to ionic elimination, the S_N2 mechanism at C-3 prevails as long as ring B remains saturated. If, however, elimination at C-6 is the first event leading to formation of the double bond between C-5 and C-6, a 3α-tosyloxy-Δ^5 compound is produced as an intermediate. The latter has the substituent at C-3 in the axial configuration and is therefore readily converted to the heteroannular diene. This has been clearly demonstrated in the case of epicholesterol tosylate (3) which on acetolysis affords quantitatively cholestadiene. It is thus obvious that increased yields of 3β-hydroxy-Δ^5 compounds must be due to an increased rate of S_N2 at C-3 or, in other words, due to a relative decreased rate of E1 at C-6. Changing the solvents as indicated above provides a reaction medium that becomes progressively more alkaline; it is well known that unimolecular eliminations proceed more readily in acid solution mainly because ionization or carbonium ion formation is the result of electrophilic attack. The increased yield of 3β-hydroxy-Δ^5 steroid is therefore ascribed to a suppression in the rate of elimination at C-6 in the strongly basic medium of aqueous dimethylformamide containing potassium acetate. Other factors such as dielectric constant of the solvent, temperature, and steric considerations enter undoubtedly into the mechanism of the reaction but it is believed that the pH of the medium is the most important contribution.

EXPERIMENTAL[2]

3α,6α,24-Trihydroxy-24,24-diphenyl-cholane (II)

A Grignard reagent was prepared from magnesium turnings (19.2 gm.) and bromobenzene (85 ml.) in tetrahydrofuran (150 ml.). There was then added a solution of methyl hyodesoxycholate benzene complex (25 gm.) in tetrahydrofuran (175 ml.) and the mixture was refluxed for 15 hr. with constant stirring. The solution was poured into ice-cold, dilute acid and the resulting precipitate was filtered off, washed with water and toluene to yield 26.2 gm. of material,

[2]*The microanalyses were kindly performed by Mr. E. Thommen, Basel, Switzerland.*

m.p. 194–201°C. The toluene extract was evaporated to dryness and the residue crystallized from acetone to provide an additional 3.2 gm. of product, m.p. 133° and 204°C. Recrystallization from benzene gave II, m.p. 204.5–206.5°C.

3α,6α-Diacetoxy-24,24-diphenyl-Δ²³-cholene (IIIb)

Compound II (8 gm.) was refluxed for five hours with acetic acid (40 ml.) and acetic anhydride (8 ml.). The solution was then poured into water and the precipitate was filtered off, washed, and dried to provide III*b* (8.93 gm.). This material was recrystallized first from aqueous acetone then from methanol to give crystals, m.p. 122–124°C. and $[\alpha]_D^{26}$ +43.6° (*c*, 1.334, dioxane).

3α,6α-Dihydroxy-24,24-diphenyl-Δ²³-cholene (IIIa)

Hydrolysis of III*b* was carried out by refluxing with 4% methanolic potassium hydroxide for two hours. The solution was poured into water and the precipitate, after being washed and dried, was recrystallized from aqueous methanol to yield nearly quantitatively III*a*, m.p. 184–186°C., $[\alpha]_D^{26}$ +36.8° (*c*, 0.891, dioxane) and $E_{1cm}^{1\%}$ 305 (λ_{max} 250 mμ).

3α,6α-Ditosyloxy-24,24-diphenyl-Δ²³-cholene (IIIc)

Compound III*a* (5 gm.) was dissolved in pyridine (20 ml.) and tosyl chloride (5.7 gm.) was added. After 48 hr. at 20°C. the excess tosyl chloride was decomposed by addition of water (2 ml.), the solution was then poured into dilute acid and extracted with ether. The solvent extract was washed with dilute acid, then with water, dried over sodium sulphate, and evaporated to a small volume. Crystallization provided 7.4 gm. of III*c*, m.p. 130–132°C. Three crystallizations from ether and iso-octane gave material, m.p. 133–135°C. and $[\alpha]_D^{23}$ +30.6° (*c*, 1.425, dioxane). Analysis: Calcd. for $C_{50}H_{60}O_6S_2$: C, 73.13; H, 7.37; S, 7.81. Found: C, 72.98, 73.00; H, 7.46, 7.52; S, 8.04, 7.99.

3α,6α-Diacetoxy-24,24-diphenyl-Δ²⁰,²³-choladiene (IVb)

Compound III*b* (5 gm.) was dissolved in hexane (60 ml.) and there was then added sodium bicarbonate (0.9 gm.), N-bromosuccinimide (1.8 gm.), and α,α′-azo-diisobutyronitrile (150 mgm.) or a 25% solution of diacetyl peroxide in dimethyl phthalate (0.2 ml.). This mixture was refluxed for one hour while being stirred vigorously. The precipitated succinimide was then removed by filtration and the filtrate added to acetic acid (55 ml.) containing sodium acetate (5 gm.). After removal of hexane by distillation, the solution was refluxed for one-half hour and finally poured into water to provide, after filtration and drying, 4.96 gm. of crude IV*b*. This material had $E_{1cm}^{1\%}$ 398 (λ_{max} 306 mμ), indicating a yield of 85.6%. Repeated recrystallization from methanol and ethyl acetate afforded pure IV*b*, m.p. 125–126°C., $[\alpha]_D^{24}$ +49.2° (*c*, 2.344, chloroform), $[\alpha]_D^{24}$ +35.1° (*c*, 3.126, dioxane), and $E_{1cm}^{1\%}$ 462 (λ_{max} 306 mμ). This compound gave a green color with trichloroacetic acid, a deep brown with tetranitromethane, and a wine-red in the Liebermann–Burchard reaction. Analysis: Calcd. for $C_{40}H_{50}O_4$: C, 80.77; H, 8.47. Found: C, 80.85, 80.83; H, 8.79, 8.72.

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3α,6α-Dihydroxy-24,24-diphenyl-Δ^{20,23}-choladiene (*IVa*)

The diacetate (IV*b*) was saponified by refluxing with 4% methanolic potassium hydroxide. Repeated alternate recrystallization from benzene and aqueous methanol yielded IV*a*, m.p. 211.5–216°C., $[\alpha]_D^{24}$ +48.5° (*c*, 2.579, chloroform) and $E_{1cm}^{1\%}$ 555 (λ_{max} 306 mμ). Analysis: Calcd. for $C_{36}H_{46}O_2$: C, 84.66; H, 9.08. Found: C, 84.71, 84.70; H, 9.08, 9.10.

3α,6α-Ditosyloxy-24,24-diphenyl-Δ^{20,23}-choladiene (*IVc*)

Compound IV*a* (2 gm.) dissolved in pyridine (10 ml.) was treated with tosyl chloride (1.8 gm.). After 48 hr. at 20°C., the excess reagent was decomposed by addition of ice, the mixture was poured into dilute acid and extracted with chloroform. The solvent extract was washed, dried, and evaporated leaving a residue which crystallized from ether to give 2.9 gm. (91%) of IV*c*, m.p. 149–151°C. Two further recrystallizations from ether gave material, m.p. 156–157°C. (decomp.) and $[\alpha]_D^{20}$ +26.2° (*c*, 1.44, dioxane). Analysis: Calcd. for $C_{50}H_{58}O_6S_2$: C, 73.31; H, 7.14; S, 7.83. Found: C, 73.26, 73.20; H, 7.19, 7.23; S, 8.05, 7.99.

3α,6α-Dihydroxy-pregnan-20-one (*VIIIa*)

A solution of IV*b* (17.7 gm.) in chloroform (200 ml.) and 80% acetic acid (220 ml.) was cooled to 0°C. and there was then added within one-half hour 80% acetic acid (200 ml.) containing chromic acid (12.3 gm.). The solution was stirred at 0°C. for four hours, the excess oxidizing agent was destroyed by addition of sodium bisulphite, and the solvents were evaporated *in vacuo*. The residue was diluted with water and extracted with ether, the solvent extract was washed and taken to dryness.

Hydrolysis of the residue with methanol (300 ml.) and concentrated hydrochloric acid (5 ml.) at 20°C. for 14 hr. was followed by neutralization with sodium bicarbonate. The methanol was evaporated and the residue taken up in ether–chloroform and saturated salt solution. The solvent extract was washed once more with salt solution, dried, and evaporated. The residue was dissolved in hot benzene (100 ml.), the solution cooled, the precipitate filtered off and dried to provide 7.82 gm. (78%) of crystals, m.p. 90–95° and 179–181°C. Recrystallization from ethyl acetate afforded VIII*a*, m.p. 192–193°C. and $[\alpha]_D^{24}$ +69.7° (*c*, 1.597, dioxane). Analysis: Calcd. for $C_{21}H_{34}O_3$: C, 75.40; H, 10.25. Found: C, 75.26, 75.23; H, 10.30, 10.37.

3α,6α-Ditosyloxy-pregnan-20-one (*VIIIc*)

Compound VIII*a* (2.5 gm.) was treated in the usual manner with pyridine (10 ml.) and tosyl chloride (4.2 gm.). The reaction mixture, after addition of dilute acid, was extracted with ether and the solvent extract worked up to give a residue which crystallized from ether to afford VIII*c* (3.93 gm.; 82%), m.p. 140–142°C. Two further recrystallizations from ether gave material, m.p. 147–148°C. and $[\alpha]_D^{24}$ +34° (*c*, 1.342, dioxane). Analysis: Calcd. for $C_{35}H_{46}O_7S_2$: C, 65.39; H, 7.21; S, 9.98. Found: C, 65.45, 65.43; H, 7.37, 7.32; S, 9.69, 9.75.

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3α,6α-Dihydroxy-pregnan-20-one Ethylene Ketal (IXa)

The ketone VIII*a* (3.06 gm.) was dissolved in dry benzene (100 ml.) and ethylene glycol (6 ml.). After addition of *p*-toluenesulphonic acid monohydrate (150 mgm.), the mixture was stirred and refluxed for four hours, during which time water was continually removed by the use of a Dean-Stark trap. On cooling, saturated sodium bicarbonate solution (2 ml.) was added and the solvents were evaporated *in vacuo*. The solid residue was shaken with saturated salt solution, filtered off, washed with water, and dried to furnish 3.34 gm. (98%) of material, m.p. 218–228°C. Recrystallization from methanol afforded pure IX*a*, m.p. 227–228°C. and $[\alpha]_D^{26}$ +6.44° (*c*, 1.63, pyridine). Analysis: Calcd. for $C_{23}H_{38}O_4$: C, 72.97; H, 10.11. Found: C, 72.81, 72.86; H, 10.07, 10.03.

Acetylation of IX*a* provided the corresponding diacetate (IX*b*), crystallized from aqueous methanol, m.p. 125–132°C. Two recrystallizations from the same solvent yielded material, m.p. 139–140°C. and $[\alpha]_D^{24}$ +15.03° (*c*, 1.55, pyridine). Analysis: Calcd. for $C_{27}H_{42}O_6$: C, 70.10; H, 9.15. Found: C, 69.84, 70.04; H, 9.32, 9.40.

3α,6α-Ditosyloxy-pregnan-20-one Ethylene Ketal (IXc)

Tosylation of IX*a* (0.9 gm.) with pyridine (6 ml.) and tosyl chloride (1.4 gm.) was carried out as described above. The products were taken up in ethylene dichloride and the solvent extract was washed, dried, and evaporated. From ether, crystals of IX*c* (1.42 gm.; 87%), m.p. 147–148°C., were deposited. Crystallization from benzene–hexane raised the m.p. to 151.5–152°C. and this sample then had $[\alpha]_D^{24}$ +5.21° (*c*, 1.515, pyridine). Analysis: Calcd. for $C_{37}H_{50}O_8S_2$: C, 64.72; H, 7.28; S, 9.32. Found: C, 64.60, 64.59; H, 7.58, 7.35; S, 9.16.

Pregnenolone Ethylene Ketal (X)

Compound IX*c* (8 gm.) was dissolved in dimethylformamide (85 ml.) and treated with a solution of potassium acetate (12 gm.) in water (20 ml.). The solution was kept at 95°C. for four hours. After complete removal of the solvents *in vacuo*, the residue was saponified by refluxing with methanolic potassium hydroxide. Part of the methanol was evaporated, the residue was diluted with water, cooled, and the resulting precipitate was filtered off. Thorough washing and drying gave a residue (4.38 gm.), m.p. 107–125°C. This was recrystallized repeatedly from methanol containing a few drops of pyridine to yield a pure sample of X, m.p. 164–167°C. and $[\alpha]_D^{24}$ −30.6° (*c*, 1.86, pyridine). Analysis: Calcd. for $C_{23}H_{36}O_3$: C, 76.62; H, 10.07. Found: C, 76.62, 76.54; H, 10.16, 10.17.

Progesterone 20-Ethylene Ketal (XI)

A solution of X (3.5 gm.) in toluene (100 ml.) and cyclohexanone (30 ml.) was distilled briefly to remove traces of moisture and, after addition of aluminum isopropoxide (2 gm.), the solution was refluxed for one hour. The mixture was treated with water (20 ml.), the solvents were removed *in vacuo*, and the residue was taken up in benzene. The solvent extract was filtered and

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evaporated to give a solid which was leached with hexane and filtered off to yield 3.25 gm. (93%) of crude XI, m.p. 184–189°C. Recrystallization from ethyl acetate provided material, m.p. 189–191°C., $[\alpha]_D^{24}$ +97.5° (*c*, 1.13, pyridine), and $E_{1cm}^{1\%}$ 447 (λ_{max} 242 mμ). Analysis: Calcd. for $C_{23}H_{34}O_3$: C, 77.05; H, 9.56. Found: C, 77.04, 77.11; H, 9.61, 9.59.

Progesterone (XII)

Compound XI (2 gm.) was dissolved in acetone (30 ml.) and water (3 ml.) by warming briefly and, after addition of *p*-toluenesulphonic acid (100 mgm.), the solution was kept at 20°C. for 15 hr. The acetone was then evaporated, the residue was treated with a dilute solution of sodium bicarbonate, and the precipitate was filtered off, washed with water, and dried. This product (1.82 gm.), m.p. 117–128°C., was crystallized from aqueous acetone to provide progesterone, m.p. 131–133°C., $[\alpha]_D^{24}$ +177.2° (*c*, 2.5, dioxane).

Methyl Hyodesoxycholate Ditosylate (Ic)

Methyl hyodesoxycholate (25 gm.) was dissolved in dry pyridine (50 ml.) and tosyl chloride (28.8 gm.) was added. The solution was kept at room temperature for two days. Subsequently, the mixture was cooled, the excess reagent was decomposed by ice, and the solution was poured into ice-cold, dilute hydrochloric acid. After the mixture was stirred for one-half hour, the precipitate was filtered, washed with water, and dried to yield 43.9 gm. of material. Recrystallization from ethyl acetate afforded 41.6 gm. (95%) of I*c*, m.p. 165–167°C. and $[\alpha]_D^{24}$ +9.8° (*c*, 1.016, dioxane). Analysis: Calcd. for $C_{39}H_{54}O_8S_2$: C, 65.53; H, 7.61; S, 8.97; OCH_3, 4.34. Found: C, 65.60, 65.55; H, 7.68, 7.65; S, 9.19; OCH_3, 4.50.

3β-Hydroxy-Δ⁵-cholenic Acid (V)

A solution of potassium acetate (7.3 gm.) in water (3.5 ml.) and dimethylformamide (40 ml.) was heated to 100–105°C. After addition of I*c* (5 gm.), the solution was kept at the above temperature for five hours. It was then poured into cold, dilute hydrochloric acid and the resulting precipitate was filtered off and washed with water. The wet solid was saponified by refluxing with 4% methanolic potassium hydroxide (70 ml.) for two hours. The solution was poured into dilute acid, the precipitate was filtered, washed, and dried. Recrystallization from ethyl acetate yielded 1.92 gm. (73%) of product, m.p. 220–227°C. Two crystallizations from acetic acid gave pure V, m.p. 230–233°C., giving an insoluble digitonide and a yellow coloration with tetranitromethane. The identity of V was conclusively established by melting point and mixed melting point of the corresponding methyl ester and methyl ester acetate.

The filtrate was evaporated to dryness to leave a residue (0.71 gm.) which was found, by ultraviolet absorption measurement at 235 mμ, to contain 0.3 gm. of choladienic acid.

3β-Hydroxy-24,24-diphenyl-Δ⁵,²³-choladiene (VI)

The dehydrotosylation of III*c* (5 gm.) was carried out under the conditions described in the preceding experiment. After saponification and crystallization of the residue from acetone, there was obtained 1.95 gm. of crystals, m.p.

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164–170°C. Recrystallization from the same solvent gave a pure sample of VI, m.p. 176–179°C.

3β-Hydroxy-24,24-diphenyl-$\Delta^{5,20,23}$-cholatriene (VII)

Compound IV*c* (81.5 gm.) was dehydrotosylated in the manner set forth for the preparation of V. Following saponification, the reaction products were crystallized from ethanol to give 38.5 gm. (78%) of VII, m.p. 130–137°C. Recrystallization from hexane, then from ethanol, gave m.p. 157–161°C.

A sample of VII (1 gm.) dissolved in ethyl acetate (15 ml.) was added to a warm solution of anhydrous oxalic acid (0.2 gm.) in ethyl acetate (2 ml.). A precipitate formed at once; after refrigeration, the crystals were filtered off, washed with ethyl acetate, and dried to yield 0.95 gm. of the adduct. Three recrystallizations from ethyl acetate provided a pure sample of the adduct, m.p. 192–195°C. and $[\alpha]_D^{20}$ −14.2° (*c*, 1.01, dioxane). Analysis: Calcd. for $C_{36}H_{44}O.\frac{1}{2}C_2H_2O_4$: C, 82.64; H, 8.44. Found: C, 82.53, 82.63; H, 8.56, 8.63.

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STUDIES IN THE WAGNER–MEERWEIN REARRANGEMENT. PART I[1]

By F. A. L. Anet and P. M. G. Bavin[2]

ABSTRACT

The preparation by a convenient route of 9-methyl, ethyl, isopropyl, *t*-butyl, and benzyl phenanthrenes is described. This consists of the alkylation of methyl fluorene-9-carboxylate under mild conditions, reduction of the ester group with lithium aluminum hydride, and then tosylation of the carbinol. The tosyl esters so prepared rearrange to alkylphenanthrenes with simultaneous loss of the elements of toluenesulphonic acid, when heated alone or in formic acid. Dehydration of the carbinols at 160° with polyphosphoric acid also promotes rearrangement.

Application of the Wagner–Meerwein rearrangement to the synthesis of polycyclic hydrocarbons and their derivatives has received little attention. The first recognized example reported (2) was the dehydration and rearrangement of 9-phenyl-9-(α-hydroxybenzyl)-fluorene to 9,10-diphenylphenanthrene under the influence of iodine in acetic acid. The same product had been obtained earlier by the reduction of 9-phenyl-9-benzoylfluorene with red phosphorus and iodine (34).

More recently, phenanthrene has been obtained from 9-fluorenylmethanol (7), and this has been extended to the preparation of phenanthrene-(9,10-$^{14}C_1$) (13), 1,2-benzanthracene-(5,6-$^{14}C_1$) (14), and chrysene-(5,6-$^{14}C_1$) (15). 2,7-Dibromophenanthrene has also been prepared from the appropriate fluorene derivative (9). In all of these examples, phosphorus pentoxide in boiling xylene was used to effect rearrangement.

Polyphosphoric acid at 160° has been used to bring about the rearrangement of 9-fluorenylmethyl acetate and its 2-nitro derivative to give phenanthrene and 2-nitrophenanthrene, respectively, in good yield (3).

Two types of fluorene derivatives capable of undergoing the Wagner–Meerwein rearrangement are distinguished, differentiated by the 9-carbon atom being respectively tertiary and quaternary, I and II. Compounds of type I may give derivatives of both phenanthrene and dibenzfulvene, whilst those of type II may give only the former. Migration of the group R in compounds of type II has not been observed. Conditions under which the different products are obtained have been studied (17), and it was found that the best yields of phenanthrene derivatives were obtained by using phosphorus pentoxide in boiling xylene.

As a preliminary to the study of more complex systems, we have made a detailed examination of a convenient route to the 9-alkylphenanthrenes. This is based on methyl fluorene-9-carboxylate, the parent acid of which is simply prepared from benzilic acid (29), in contrast to a recent statement in the

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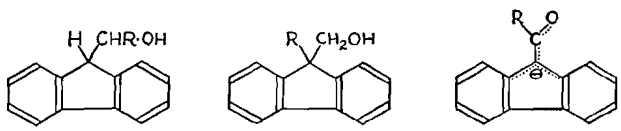
Contribution from the Department of Chemistry, University of Ottawa, Ottawa, Ontario. Presented in part before the Annual Meeting of L'Association canadienne-française pour l'avancement des sciences, Ottawa, November, 1955.
[2]*National Research Council Postdoctorate Fellow, 1954–56.*



I II III

literature (33). The acidity of the 9-hydrogen of this ester has been known for some time (33, 35, 38, 39; see also 16, 17, 28), and 9-alkyl derivatives of the (ethyl) ester were prepared by Wislicenus (38, 39). The ester has also been utilized in the Michael reaction (11, 31, 33, 36). 9-Formylfluorene and related compounds have been alkylated (8).

Methyl fluorene-9-carboxylate and its amide are soluble in aqueous alcohol containing strong alkali to give yellow solutions which show a pale blue fluorescence. These solutions are thought to contain the anion III, where R is $-OCH_3$ or $-NH_2$. The existence of the anion is well illustrated in Fig. 1, which

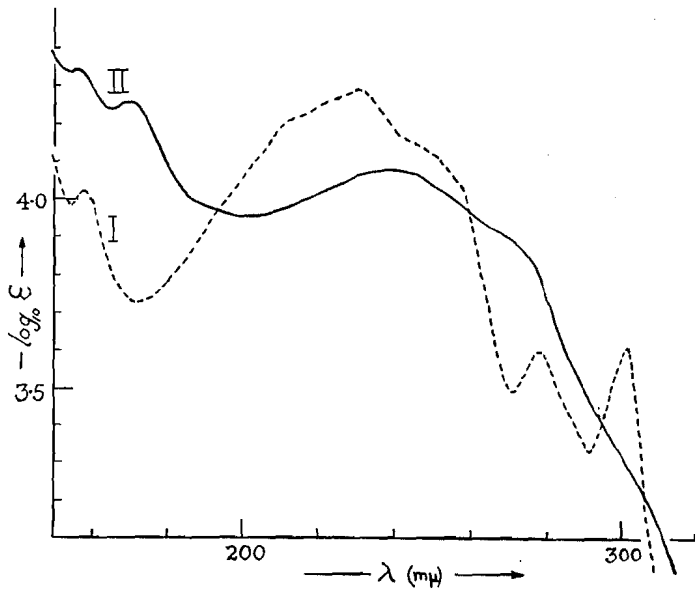


FIG. 1.

shows the ultraviolet spectra of methyl fluorene-9-carboxylate in methanol (I) and in methanolic sodium methoxide (II). It is concluded that conversion to the anion was almost complete under the conditions employed, a view which is supported by the failure of the ester to undergo base-catalyzed transesterification under conditions where the 9-methyl derivative showed this reaction (see below).

Alkylation of methyl fluorene-9-carboxylate proceeded smoothly in dry methanol in the presence of excess sodium methoxide and alkyl halide. In this

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way we prepared the 9-methyl, ethyl, propyl, isopropyl, allyl, butyl, *s*-butyl, *t*-butyl, octyl, cyclohexyl, and benzyl derivatives, all but the octyl being obtained crystalline. This procedure is very much more convenient than that employed by Wislicenus (38, 39), who used the ethyl ester and excess potassium as base. The latter ester gives rise to low-melting derivatives, making their isolation and purification in good yield difficult. We obtained methyl 9-*t*-butylfluorene-9-carboxylate in 94% yield, in striking contrast to the *t*-butylation of malonic ester and related compounds which gives negligible yields.

Methyl 9-methylfluorene-9-carboxylate underwent base-catalyzed transesterification under conditions as mild as those used for the alkylations, but the highly hindered 9-*t*-butyl derivative did not do so to a demonstrable extent.

Reduction of the 9-alkyl esters by lithium aluminum hydride proceeded smoothly, although an extended reaction time was necessary in the case of the *t*-butyl derivative to ensure complete reaction. The 9-alkyl-9-fluorenylmethanols so prepared were readily tosylated, giving easily crystallized esters.

Conversion to the 9-alkylphenanthrenes was effected in three ways: *A*, the carbinol was heated with polyphosphoric acid at 160°; *B*, the tosyl ester was boiled under reflux for a few minutes with formic acid; *C*, the tosyl ester was heated to its melting point. *B* was the most convenient method. We prepared the known 9-methyl, ethyl, isopropyl, and benzyl phenanthrenes, as well as the previously unknown and difficultly accessible 9-*t*-butylphenanthrene. It is concluded that the method is of wide applicability.

9-*t*-Butyl-9-fluorenylmethanol gave some unexpected results. Treatment by method *A* gave a mixture of phenanthrene and 9-*t*-butylphenanthrene, together with a trace of a third compound, the presence of which prevented an analysis of the mixture being made from its ultraviolet spectrum. By starting with pure methyl fluorene-9-carboxylate and carefully purifying the derivatives, we satisfied ourselves that the phenanthrene did not arise from 9-fluorenylmethanol present as an impurity. Additional experiments showed that 9-*t*-butylphenanthrene was stable in polyphosphoric acid at 200°, and that phenanthrene was not alkylated by *t*-butyl alcohol under similar conditions.

There can be little doubt that the rearrangement of 9-fluorenylmethanol and its derivatives takes place through an intermediate carbonium ion, in a manner analogous to more classical examples[3] (19, page 474 ff.; see also 17). The formation of phenanthrene from 9-*t*-butyl-9-fluorenylmethanol may be formulated as shown (Fig. 2), this mechanism accounting for the formation of phenanthrene on the basis of the stability of the *t*-butyl carbonium ion.

Wittig (40) found that treatment of 9-benzyl-9-fluorenylmethanol at 100° with phosphorus tribromide gave an excellent yield of 9-benzylphenanthrene. We have found that 9-*t*-butyl-9-fluorenylmethanol when treated with phosphorus trichloride under similar conditions does not give 9-*t*-butylphenanthrene. Instead a crystalline derivative of m.p. 145° was obtained. This had a typical fluorene spectrum (12, 20) and was soluble in aqueous potassium hydroxide; it reprecipitated on acidification. When boiled with formic acid

[3]*Wittig and co-workers recently obtained 9-benzylphenanthrene in good yield when 9-benzyl-9-fluorenylmethyl bromide was treated with ethereal lithium phenyl (40). This reaction cannot be formulated as a simple Wagner–Meerwein rearrangement.*

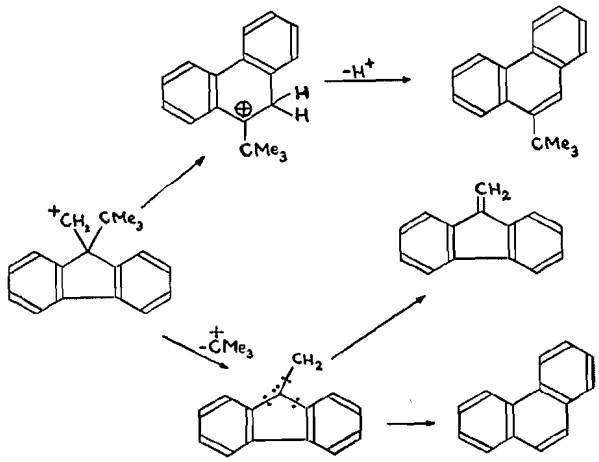

FIG. 2.

for a few minutes, it gave 9-*t*-butylphenanthrene. These properties and elementary analyses show it to be the phosphite, RO.P(OH) : O. Its isolation and rearrangement suggest that similar esters are intermediates in those rearrangements brought about by phosphorus pentoxide or polyphosphoric acid, such esters, like the tosylates, tending to undergo solvolysis by an S_N1 process. Heating 9-*t*-butyl-9-fluorenylmethanol with formic acid gave only the formate, although under similar conditions trichloracetic acid gave some 9-*t*-butylphenanthrene.

Mild hydrolysis of the methyl 9-alkylfluorene-9-carboxylates affords the acids, more vigorous conditions giving the 9-alkylfluorenes (31). Preparation of the 9-*t*-butyl acid proved difficult, owing to the highly hindered system. Its melting point (237°) was considerably higher than that reported earlier (16, 224–226°), and it exists in at least two crystalline forms. Dimorphism was also observed with 9-allylfluorene-9-carboxylic acid. The previously unknown 9-*t*-butylfluorene has now been prepared.

In a recent communication (24), the phenylation of diethyl ketone was described, using sodamide and bromobenzene in liquid ammonia. Attempts to prepare methyl 9-phenylfluorene-9-carboxylate by a similar procedure have failed, a small quantity of what is probably 9,9′-difluorenyl being isolated.

Attempts to prepare 9-phenylphenanthrene from the readily accessible 9-(α-hydroxybenzyl)-fluorene failed. The latter compound was obtained in good yield from 9-benzoylfluorene by reduction with potassium borohydride. The reduction did not proceed in the presence of an excess of strong alkali, owing to the formation of the anion (III, R is phenyl) as shown by the deep yellow color of the solution. Treatment of the carbinol with polyphosphoric acid did not give 9-phenylphenanthrene, giving instead 9-benzalfluorene. The ultraviolet spectrum was in agreement with this structure for the product (25).

Recently, Martin and co-workers (26) have reported the results of solvolytic studies on 9-fluorenylmethyl esters. The trichloracetate, for example, was found

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to undergo solvolysis in neutral aqueous solution by a unimolecular mechanism involving alkyl–oxygen fission. The product isolated was 9-fluorenylmethanol, from which it was concluded that the 9-fluorenylmethyl cation reacted much faster with the solvent than it rearranged, in contrast to the 9-alkyl-9-fluorenylmethyl cations reported in this paper. The work of Martin suggested that the solvolysis of 9-fluorenylmethyl tosylate would not give phenanthrene, the parent alcohol being the expected product.

We have made repeated attempts to prepare 9-fluorenylmethyl tosylate, but the elementary analyses have been consistently low for carbon. The ultraviolet spectrum of the products obtained by boiling the tosylate with formic acid or neutral aqueous dioxane showed the presence of a considerable proportion of phenanthrene. Additional experiments showed that the phenanthrene did not arise from 9-fluorenylmethanol.

The tosylate of 9-hydroxymethylenefluorene has been prepared, but could not be made to undergo rearrangement.

Attempts have been made to prepare fluorene-9-carboxylic acid from benzilic acid without the use of aluminum chloride. Treatment with polyphosphoric acid at 180° gave a small yield of the desired product. Attempted tosylation of benzilic acid gave benzilide in excellent yield, probably through the mixed anhydride of benzilic and toluenesulphonic acids. This view is supported by the failure of methyl benzilate to react. Treatment of benzilic acid or its methyl ester with anhydrous hydrogen fluoride gave none of the desired products.

This work is being actively continued. The ultraviolet spectra of the 9-alkylphenanthrenes will be reported shortly.

EXPERIMENTAL

All melting points are uncorrected. Values below 200° were recorded in capillaries (oil bath); those above 200° were obtained using a hot-stage microscope. Ultraviolet spectra were measured in ethanol with a Beckmann DK.2 self-recording spectrophotometer. Microanalyses are by Geller Laboratories, New Jersey, U.S.A.

Methyl Fluorene-9-carboxylate

Fluorene-9-carboxylic acid was prepared from benzilic acid (29), the scale being increased fourfold.

The dried acid (1 part) and dry methanol (15 vol.) were boiled under reflux for two hours with a catalytic amount of concentrated sulphuric acid. The volume was then reduced by a half by slow distillation, made up by the addition of fresh methanol, and the mixture again boiled for two hours. After cooling, the acid was neutralized by the cautious addition of solid sodium bicarbonate and the solution filtered. Evaporation of the filtrate gave an oil which was dissolved in the minimum of benzene–hexane (1:2) and passed through a column of activated alumina. Further elution with hexane and evaporation of the combined eluants, followed by crystallization from methanol, gave large pale yellow prisms, m.p. 64–65° (reported m.p. 66.5° (5); 63–66° (33)), raised to 65° by a further crystallization. The yield of once-crystallized material was 71–84% based on benzilic acid.

The ester was readily soluble in aqueous alcohol containing sodium hydroxide to give a yellow solution having a pale blue fluorescence. Acidification of a freshly prepared solution gave the ester unchanged.

The ester (1 gm.) was dissolved in anhydrous ethanol (50 ml.) containing sodium ethoxide from 1 gm. of sodium. After it had been left at room temperature for 24 hr., the solution was acidified and the product isolated with chloroform. Crystallization from methanol gave the ester unchanged (0.8 gm.), m.p. and mixed m.p. 64–65°.

The amide was prepared by boiling the ester (0.5 gm.) in ethylene glycol (30 ml.) with ammonia (4 ml., d. 0.88) for two hours. Small quantities of ammonia were added from time to time. On cooling, long colorless silky needles (0.2 gm.) separated. After recrystallization from ethanol (Norit) these had m.p. 253°. (Reported m.p. 251° (30).) A solution in ethanolic sodium hydroxide was yellow.

The ester formed a *1,3,5-trinitrobenzene complex*, yellow needles from methanol, m.p., 97–97.5°. Calc. for $C_{21}H_{15}O_8N_3$: C, 57.73; H, 3.44; N, 9.52. Found: C, 57.67; H, 3.46; N, 9.61%.

Preparation of the Methyl 9-Alkylfluorene-9-carboxylates

Methyl 9-Methylfluorene-9-carboxylate

Methyl fluorene-9-carboxylate (4.5 gm.) was dissolved in methanolic sodium methoxide, prepared from sodium (1.9 gm., 4.5 at. equiv.) and dry methanol (50 ml.). Methyl iodide (10 ml.) was added and the solution left overnight at room temperature. Access to moisture was prevented by a calcium chloride guard tube. Next morning, the solution was poured into cold dilute hydrochloric acid and the product isolated with chloroform. Crystallization from chloroform–hexane gave slightly yellow prisms, m.p. 108–109°, (4.2 gm., 92%). Further crystallizations gave colorless prisms of the same m.p. (Recorded m.p. 108–109° (31).)

Hydrolysis of the ester (1 gm.) for a few minutes at 50° in aqueous ethanol containing potassium hydroxide (2 gm.) gave 9-methylfluorene-9-carboxylic acid (0.6 gm.). Recrystallization from methanol gave long needles, m.p. 170–171°. (Recorded m.p. 168° (35); 168–169° (31); 170–171° (18).)

Ethyl 9-Methylfluorene-9-carboxylate

(*a*) The alkylation was carried out as described above except that ethanol replaced the methanol. The product was an oil which slowly crystallized when kept with hexane in the ice chest. Recrystallization from hexane and collection in a precooled funnel gave needles, m.p. 31°, (2.7 gm.). (Reported m.p. 33° (38).)

(*b*) Methyl 9-methylfluorene-9-carboxylate (1 gm.) was dissolved in ethanolic sodium ethoxide (from 1 gm. of sodium). After 24 hr., the product was isolated in the usual way and crystallized from hexane to give needles (0.8 gm.), m.p. 30–31°, undepressed when mixed with the sample prepared by method (*a*).

Hydrolysis of the samples prepared by both methods gave 9-methylfluorene-9-carboxylic acid, m.p. and mixed m.p. 169–170°.

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Methyl 9-Ethylfluorene-9-carboxylate

This compound was prepared as described for the methyl analogue from the ester (4.5 gm.), sodium (1 gm., 2.3 equiv.), and ethyl iodide (12 ml.). Crystallization from hexane gave long colorless prisms (4.4 gm., 86%), m.p. 79–81°. An analytical specimen was obtained after three further crystallizations, m.p. 81.5–82.0°. Calc. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 81.0; H, 6.42%.

Methyl 9-Allylfluorene-9-carboxylate

This was prepared as described for the methyl analogue from the ester (5 gm.), sodium (1.5 gm., 3 equiv.), and allyl bromide (12 ml.). Allyl chloride proved less satisfactory. Crystallization from methanol gave soft blades (5 gm., 85%), m.p. 72–74°, raised to 75° by a further crystallization. Calc. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.75; H, 6.31%.

Hydrolysis as for the methyl analogue and crystallization from hexane gave 9-allylfluorene-9-carboxylic acid as prisms, m.p. 132–132.5°. On the hot stage the acid melted at 120°, recrystallized at 126°, and finally melted at 134–136°. This sequence was observed once in the capillary m.p. apparatus. (Reported m.p. 131.5–132.5° (1).)

Methyl 9-Propylfluorene-9-carboxylate

(*a*) This was prepared as described for the methyl analogue from the ester (1.1 gm.), sodium (0.4 gm., 3 equiv.), and propyl bromide (7 ml.). Two crystallizations from methanol gave long white needles (0.87 gm., 67%), m.p. 85–85.5°. Calc. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.5; H, 6.96%.

(*b*) The 9-allyl ester (0.39 gm.) was hydrogenated in ethanol over 10% palladium-on-charcoal. Hydrogen (39.7 ml. at 21° and 733 mm. partial pressure, 1.07 moles) was absorbed in five minutes. Crystallization of the product from hexane gave needles (0.365 gm., 92%), m.p. 85°, not depressed when mixed with the sample prepared by method (*a*).

Methyl 9-Isopropylfluorene-9-carboxylate

This was prepared as described for the methyl analogue from the ester (5 gm.), sodium (1.5 gm., 3 equiv.), and isopropyl bromide (10 ml.). The product crystallized as prisms from methanol (4.8 gm., 81%), m.p. 78–79°, raised to 79–80° by successive crystallizations from methanol and acetone. Calc. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.33; H, 6.75%.

Methyl 9-Butylfluorene-9-carboxylate

This was prepared as described for the methyl analogue from the ester (1.5 gm.), sodium (0.2 gm., 1.3 equiv.), and butyl iodide (4 ml.). The product slowly crystallized when kept in the ice chest for a few days. Recrystallization was difficult but two crystallizations from ice-cold methanol with seeding gave long colorless needles, m.p. 34–34.5°. Calc. for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.45; H, 7.30%.

Methyl 9-s-Butylfluorene-9-carboxylate

This was prepared as described for the methyl analogue from the ester (1.5 gm.), sodium (0.5 gm., 3.3 equiv.), and *s*-butyl bromide (8 ml.). Crystal-

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lization from methanol (Norit) and subsequent crystallizations from methanol and acetone gave colorless prisms and rectangular tablets (1.1 gm., 59%), m.p. 70–71°. Under the microscope, the crystals showed extensive twinning. Calc. for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.6; H, 7.3%.

Methyl 9-t-Butylfluorene-9-carboxylate

This was prepared as described for the methyl analogue from the ester (15 gm., m.p. 65°), sodium (6 gm., 4 equiv.), and freshly prepared *t*-butyl bromide (40 ml.). Tertiary butyl chloride proved less satisfactory. When the alkyl halide was added, the solution turned bright orange-red, the color fading overnight. Crystallization from methanol–acetone (10:1) afforded thick prismatic needles (13.3 gm., 71%), m.p. 113°, not raised by further crystallizations. Concentration of the mother liquors gave a second crop, m.p. 110–112°, (2.1 gm., bringing the yield up to 94%).

The infrared spectrum was measured in carbon tetrachloride solution and showed sharp bands at 1368 and 1401 $cm.^{-1}$ with the former the more intense. (Bellamy (4, p. 23) records 1365 and 1395 $cm.^{-1}$ for the *t*-butyl group, the bands having the same intensity distribution.) Calc. for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.33; H, 7.24%.

The ester was recovered unchanged after treatment with ethanolic sodium ethoxide under the conditions used for the methyl analogue. Hydrolysis was slow, 9-*t*-butylfluorene-9-carboxylic acid being prepared as follows: the ester (1 gm.) was dissolved in ethanol (50 ml.) and a solution of potassium hydroxide (5 gm.) in water (40 ml.) added. The solution was maintained at 80–85° for three hours, small quantities of ethanol being added at intervals to maintain homogeneity. After the solution had been cooled, ethanol was removed by evaporation and the solution extracted with hexane. The aqueous layer was acidified, giving 9-*t*-butylfluorene-9-carboxylic acid (0.6 gm.). Crystallization from methanol gave prisms and rhombs, which partially melted at 233–235°, recrystallized as irregular prisms, and finally melted at 237°. (Reported m.p. 224–226° (16).[4])

9-t-Butylfluorene

Methyl 9-*t*-butylfluorene-9-carboxylate (0.305 gm.) was boiled under reflux with ethylene glycol (30 ml.) and a solution of potassium hydroxide (2 gm.) in water (2 ml.). The solution rapidly turned yellow, becoming colorless after two hours, during which time a white solid collected in the condenser. The solid was crystallized from methanol, giving white needles (0.105 gm.), m.p. 101°, raised to 101.5° by a further crystallization. The mixed m.p. with fluorene (m.p. 115°) was 75–80°. Calc. for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.99; H, 8.16%.

Methyl 9-Octylfluorene-9-carboxylate

This was prepared as described for the methyl analogue from the ester (1.5 gm.), sodium (0.17 gm.), and octyl bromide (6 ml.). The product was

[4]*The discrepancy in the melting point may be due to polymorphism, or possibly due to the fact that the microscope slides are soft glass whilst capillaries are usually Pyrex, surface alkali then being responsible for the variation.*

distilled in a Späth bulb at 1–2 mm., giving a pale yellow oil, b.p. 175–190°, (4.2 gm.), and an almost colorless oil, b.p. 190–200°, (1.5 gm.). Calc. for $C_{23}H_{28}O_2$: C, 82.10; H, 8.39. Found: C, 81.72; H, 8.37%.

Methyl 9-Cyclohexylfluorene-9-carboxylate

This was prepared as described for the methyl analogue from the ester (1.5 gm.), sodium (0.5 gm., 3 equiv.), and cyclohexyl bromide (8 ml.). Crystallization from methanol (Norit) and two further crystallizations from acetone gave small glistening prisms, m.p. 121°, (1.6 gm., 76%). Calc. for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.31; H, 7.32%.

Methyl 9-Benzylfluorene-9-carboxylate

This was prepared as described for the methyl analogue from the ester (5 gm.), sodium (1.5 gm., 3 equiv.), and benzyl chloride (12 ml.). Crystallization from methanol–acetone (1:4) gave large pale yellow prisms and rhombs (5.55 gm., 79%), m.p. 71–73°. Two further crystallizations from acetone (Norit) gave colorless prisms, m.p. 74–75°. Calc. for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 84.46; H, 6.04%.

Preparation of the 9-Alkylphenanthrenes

9-Methylphenanthrene

9-Methyl-9-fluorenylmethanol

This was prepared from the appropriate ester (2.5 gm.) by reduction with lithium aluminum hydride (1.5 moles). The product was crystallized from hexane, giving prismatic needles (2.1 gm., 95%), m.p. 147°. (Reported m.p. 148–149° (17).)

9-Methyl-9-fluorenylmethyl Tosylate

The preceding carbinol (4 gm.) was dissolved in dry pyridine (30 ml.) containing *p*-toluenesulphonyl chloride (1.1 moles). After it had been left for 18 hr. at room temperature, the solution was poured into excess cold dilute hydrochloric acid and the product isolated with chloroform. Crystallization from benzene-heptane (1:5) gave colorless needles (4.2 gm.), m.p. 103–104°. Calc. for $C_{22}H_{20}O_3S$: C, 72.50; H, 5.53. Found: C, 72.59; H, 5.68%.

9-Methylphenanthrene

Method A.—The carbinol (2 gm.) and polyphosphoric acid (120 ml.) were stirred together at 160° for 30 min. After it had been cooled, the solution was poured onto ice and the product isolated with chloroform. Evaporation left a yellow oil which was chromatographed from hexane on alumina. The early fractions gave a white solid, m.p. 91–92°. Crystallization from methanol gave white needles, m.p. 92–92.5°, (1.1 gm., 60%). (Reported m.p. 90–91° (36); 92–93° (17).) The *picrate* crystallized from methanol as orange needles, m.p. 154–155°. (Reported m.p. 152–153° (36).)

Method B.—The tosyl ester (2 gm.) was boiled under reflux for a few minutes with formic acid (30 ml., 88%) and then poured into water. The product was isolated with chloroform and crystallized from methanol to give slightly yellow

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plates and prisms (1.1 gm., 80%), m.p. 91–92°, not depressed when mixed with a sample prepared by method *A*.

Method C.—The tosyl ester (0.1 gm.) was heated to its melting point and the products dissolved in ethanol (5 ml.). The ultraviolet spectrum of this solution showed that 9-methylphenanthrene had been formed in practically quantitative yield.

9-Ethylphenanthrene

9-Ethyl-9-fluorenylmethanol

This was prepared in the usual way. It crystallized from hexane as prisms (92%), m.p. 74–76°, raised to 76.5–77.0° by three further crystallizations. Calc. for $C_{16}H_{16}O$: C, 85.67; H, 7.19. Found: C, 85.85; H, 7.29%. The *tosylate* crystallized as needles from heptane (85%), m.p. 134°. Calc. for $C_{23}H_{22}O_3S$: S, 8.47. Found: S, 8.56, 8.59%.

9-Ethylphenanthrene

Method *A* gave a white solid (66%) which crystallized from methanol as small needles, m.p. 62–63°. (Recorded m.p. 62.5–63.0° (6).) The *picrate* separated as orange needles from methanol, m.p. 118–119°. (Reported m.p. 123–124° (6).) Method *B* gave pure 9-ethylphenanthrene in 87% yield, and its formation by method *C* was shown spectroscopically.

9-Isopropylphenanthrene

9-Isopropyl-9-fluorenylmethanol

This was obtained as a colorless oil which failed to crystallize. The *tosyl ester* rapidly crystallized when scratched with hexane. One crystallization from heptane gave long white needles (72% based on the carboxylic ester), m.p. 90–91°. Calc. for $C_{24}H_{24}O_3S$: C, 73.44; H, 6.16. Found: C, 73.61; H, 5.97%.

9-Isopropylphenanthrene

This was prepared by method *B* as a yellow oil. Chromatography followed by crystallization from methanol gave large hexagonal plates (52%), m.p. 41–42°. (Reported m.p. 41–42° (6).) The *picrate* separated as orange needles from methanol, m.p. 106–107°. (Reported m.p. 109–110° (6).)

9-t-Butylphenanthrene

9-t-Butyl-9-fluorenylmethanol

9-*t*-Butyl-9-fluorenylmethanol was prepared in the usual way, except that the reaction time was extended to 24 hr. Crystallization from hexane gave prismatic needles (98%), m.p. 76–77°, not raised by further crystallizations. Calc. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.86, 86.04; H, 8.12, 8.23%.

The *formate* was prepared by boiling the carbinol with formic acid for four hours. Recrystallization from methanol gave white needles, m.p. 90°. Calc. for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.1; H, 7.23%. The ultraviolet spectrum of the formic acid mother liquors remaining when the reaction time was extended to 14 hr. showed phenanthrene derivatives not to be present.

The *acetate*, prepared by esterification with acetic anhydride – sulphuric acid, crystallized from hexane as prisms, m.p. 70–71°. Calc. for $C_{20}H_{22}O_2$: C, 81.6; H, 7.53. Found: C, 81.8; H, 7.61%.

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The *tosylate* crystallized from hexane as prisms (94%), m.p. 108–110°, raised to 111° by a further crystallization. Calc. for $C_{25}H_{26}O_3S$: S, 7.89. Found: S, 7.72%.

9-t-Butyl-9-fluorenylmethyl Phosphite

The carbinol (1 gm.) and phosphorus trichloride (3 ml., from a new bottle) were heated on the steam bath in a closed vessel for two hours. After it had been cooled, the sirup was stirred with ice water and the product isolated with chloroform. It readily crystallized from methanol as large colorless prisms, m.p. 145°. Calc. for $C_{18}H_{21}O_3P$: C, 68.13; H, 6.69; P, 9.79. Found: C, 69.49; H, 6.98; P, 9.69%.

The phosphite showed a typical fluorene spectrum in the ultraviolet, and was soluble in aqueous potassium hydroxide solution; it reprecipitated upon acidification. When boiled for a few minutes with formic acid, the solution showed the characteristic ultraviolet spectrum of 9-*t*-butylphenanthrene.

9-t-Butylphenanthrene

Method A.—The carbinol (1 gm.) gave a yellow oil, which was decolorized by chromatography. The partially purified product (0.806 gm.) was transferred to a Späth bulb and maintained at 100–110° at 1–2 mm. for half an hour. A white crystalline sublimate (22 mgm.), m.p. 77–98°, was collected. Crystallization from methanol raised the m.p. to 97–99°, not depressed when mixed with phenanthrene, m.p. 99°. The ultraviolet spectrum of the sublimate was consistent with an 80% phenanthrene content.

The ultraviolet spectrum of the residue was compared with those of standard mixtures of phenanthrene and its 9-*t*-butyl derivative. It showed the presence of a further considerable quantity of phenanthrene together with 9-*t*-butylphenanthrene and a trace of a third component, the latter preventing a reliable analysis being made by this method. The residue was dissolved in methanol, filtered with a little Celite and Norit, and then seeded with 9-*t*-butylphenanthrene (below). When it was left in the ice chest overnight needles (0.4 gm.) separated, m.p. 62–64°, not depressed when mixed with 9-*t*-butylphenanthrene.

Method B gave a colorless oil which rapidly crystallized when scratched with methanol. One crystallization from methanol gave long glistening needles, m.p. 64–65°, (85%). Calc. for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.57; H, 7.77%. The *1,3,5-trinitrobenzene complex* crystallized from methanol as silky, bright yellow needles, m.p. 143°. Calc. for $C_{24}H_{21}O_6N_3$: C, 64.42; H, 4.73; N, 9.39. Found: C, 64.60; H, 5.0; N, 9.17%.

The hydrocarbon was slowly oxidized by iodic acid in boiling acetic acid, giving a small quantity of orange blades (heptane), m.p. 200–203°, not depressed when mixed with phenanthraquinone, m.p. 204°.

Method C was also shown to give 9-*t*-butylphenanthrene.

The carbinol (0.2 gm.) and trichloracetic acid (10 gm.) were heated on the steam bath for 12 hr. The solution then showed the presence of 9-*t*-butylphenanthrene by its ultraviolet spectrum. The product was isolated with chloroform and dissolved in the minimum of methanol containing trinitro-

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benzene (0.15 gm.). When this solution was cooled, yellow needles separated, m.p. 139–141°, raised to 142° when mixed with an authentic specimen of the 9-*t*-butylphenanthrene complex.

9-Benzylphenanthrene

9-Benzyl-9-fluorenylmethanol

9-Benzyl-9-fluorenylmethanol was obtained as a colorless oil (84%), a portion of which was left with hexane for several days to induce crystallization. Recrystallization from methanol gave rhombs and irregular six-sided plates, m.p. 97–98.5°. (Reported m.p. 98.5–99.0° (40).) The *tosylate* was prepared in the usual way and crystallized from heptane to give soft blades (94%), m.p. 115°. The melt almost at once recrystallized, this observation prompting the experiments under method *C*. Calc. for $C_{28}H_{24}O_3S$: C, 76.33; H, 5.49. Found: C, 76.23; H, 5.34%.

9-Benzylphenanthrene

Method B: the tosylate was boiled with formic acid, needles starting to separate within a minute. Recrystallization of the product from methanol gave colorless needles (84%), m.p. 155°. (Reported m.p. 156° (40).) *Method C*: the tosylate (0.1 gm.) was melted and the products boiled with water. The insoluble material was collected and crystallized from methanol, giving needles (0.041 gm.), m.p. and mixed m.p. with the sample from method *B*, 155°.

Attempted Preparation of 9-Phenylphenanthrene

9-(α-Hydroxybenzyl)-fluorene

9-Benzoylfluorene (37) (5.17 gm.) was boiled for half an hour with a solution of potassium borohydride (1.5 moles) in methanol–water (80 ml., 2:1). The product was crystallized from carbon tetrachloride, giving prisms (4.1 gm.), m.p. 118–119.5°. (Reported m.p. 118.5–119.0° (21).) Attempts to carry out the reduction in the presence of potassium hydroxide gave a deep yellow solution from which the color was not discharged, even on prolonged boiling.

Treatment of the carbinol with polyphosphoric acid (method *A*) gave a small yield of prisms (hexane), m.p. 70°, which had the ultraviolet spectrum of 9-benzalfluorene (25). (Reported m.p. 76° (32).)

Attempts to prepare the tosylate gave, after crystallization from benzene–hexane, a poor yield of small prisms, melting at 92–95° to a black liquid. Boiling with formic acid produced no significant change in the ultraviolet spectrum, but small prisms of m.p. 122–125° separated on cooling. These experiments were not continued.

Attempted Preparation of Methyl 9-Phenylfluorene-9-carboxylate

A solution of methyl fluorene-9-carboxylate (5 gm.) in dry ether (50 ml.) was added to a well-stirred mixture of liquid ammonia (400 ml.) containing sodamide (from 6 gm., 11 equiv., sodium). After half an hour, bromobenzene (40 ml.) was added to the orange solution which was stirred for four hours more. Ammonia was removed on the steam bath and the residue shaken with

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chloroform and water. The product was isolated from the chloroform as an orange oil. When boiled with methanol, this deposited pale buff prisms (*X*) which were collected. The filtrate was concentrated to 10 ml. and left overnight in the ice chest. Next morning, colorless needles (*Y*) were collected. No other crystalline material was obtained, but hydrolysis of the mother liquors with sodium hydroxide in aqueous ethylene glycol gave fluorene (2.9 gm.), m.p. and mixed m.p. 113–114°.

X (0.21 gm.) was insoluble in aqueous potassium hydroxide, did not contain nitrogen, and was sparingly soluble in all the common organic solvents. Attempts to sublime it at 1–2 mm. resulted in complete decomposition. Vigorous hydrolysis gave a yellow gum and a small quantity of a steam-volatile compound, the latter having a fluorene spectrum in the ultraviolet region. The dried prisms melted over a wide range.

Y (45 mgm.) was crystallized from methanol–acetone to the constant m.p. 228°. Calc. for $C_{26}H_{18}$: C, 94.51; H, 5.49. Found: C, 94.55; H, 5.77%. 9,9′-Difluorenyl has m.p. 246–247° (27). The product was very stable, subliming unchanged at one atmosphere.

9-Hydroxymethylenefluorene Tosylate

An aqueous alkaline solution of 9-formylfluorene (10) (equivalent to 0.4 gm. fluorene) was made strongly alkaline and shaken for a few minutes with tosyl chloride (1 gm.). The product was isolated with ether and crystallized from benzene–hexane, giving prismatic needles, m.p. 105–105.5°, (0.2 gm.). Calc. for $C_{21}H_{16}O_3S$: C, 72.39; H, 4.63. Found: C, 72.46; H, 4.58%. The ultraviolet spectrum was unchanged after the needles were boiled in formic acid or ethylene glycol for 12 hr., although some decomposition occurred in the latter solvent.

When the tosylate (0.99 gm.) was hydrogenated over palladium-on-charcoal, 1.1 moles of hydrogen were absorbed in 15 min. The only crystalline material isolated was the unchanged tosylate (0.1 gm.), m.p. and mixed m.p. 104–105°.

9-Fluorenylmethyl Tosylate

The following is typical of many attempts made to prepare this compound: pure 9-fluorenylmethanol (10) (3 gm.) was tosylated in the usual way, using 1.1 moles of tosyl chloride. The dried product was extracted several times with hot heptane and the amorphous residue discarded. Concentration of the extracts and filtration through Magnesol gave, on cooling, small white needles (1.15 gm.), m.p. 145°, not raised by recrystallization from the same solvent. Calc. for $C_{21}H_{18}O_3S$: C, 71.97; H, 5.18. Found: C, 69.87; H, 5.37%.

Crystallization from methanol gave similar results. Found for other samples: C, 65.32, 65.38; H, 4.90, 5.15%.

The tosylate (0.5 gm.) was boiled under reflux with formic acid for 12 hr. Aliquots were withdrawn at intervals and their ultraviolet spectra measured. They showed that phenanthrene was slowly formed, together with a fluorene derivative. Chromatography of the product followed by preparation of the

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picrate from benzene gave yellow needles (0.08 gm.). The picrate was decomposed by passage of a hexane solution over a column of activated alumina; evaporation of the eluants and two crystallizations from methanol gave a small quantity of colorless plates, m.p. 95–98°, not depressed when mixed with phenanthrene, m.p. 99°.

The tosyl ester (10.8 mgm.) and anhydrous potassium carbonate (0.2 gm.) were boiled under reflux with dioxane–water (50 ml., 1:1). Aliquots were withdrawn at intervals and the ultraviolet spectra measured, these showing the gradual appearance of the phenanthrene bands from 330 to 350 mμ which reached a constant intensity after two hours. The presence of a fluorene derivative prevented an analysis being made.

The ultraviolet spectrum of a solution of 9-fluorenylmethanol in formic acid was unchanged after prolonged boiling, with or without the addition of sulphuric acid.

Methyl 9-Bromofluorene-9-carboxylate

Treatment of methyl fluorene-9-carboxylate (1 gm.) in chloroform (10 ml.) with bromine (0.75 gm.) and four subsequent crystallizations from heptane gave needles, m.p. 121–130°, probably containing nuclear bromine.

The ester (1 gm.) and fused sodium acetate (1 gm.) were dissolved in acetic acid (15 ml.) and bromine (0.75 gm.) added. Next morning, the product was isolated with carbon tetrachloride and crystallized from hexane, giving pale yellow prisms (0.6 gm.), m.p. 106–107°. (Reported m.p. 108.5–109.0° (22).) A methanolic solution gave an instantaneous precipitate of silver bromide when treated with silver nitrate.

Experiments with Benzilic Acid

(i) A mixture of polyphosphoric acid (200 ml.) and benzilic acid (4 gm.) was stirred at 160–180° for two hours. Long slender needles (0.2 gm.) sublimed onto the sides of the vessel and were identified as fluorene-9-carboxylic acid, m.p. 226–228°; decarboxylated over copper bronze to fluorene, m.p. and mixed m.p. 114°. The mother liquors yielded benzilic acid when worked up in the usual way.

(ii) Benzilic acid (5 gm.) was tosylated in the usual way with tosyl chloride (1.1 moles) in pyridine. Crystallization of the product from benzene–hexane gave prisms (4.6 gm.), m.p. 195°, identified as benzilide. (Reported m.p. 196° (1, 23).) Attempts to tosylate methyl benzilate gave back the ester unchanged.

(iii) Treatment of benzilic acid or methyl benzilate with anhydrous hydrogen fluoride did not give detectable amounts of fluorene derivatives.

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THE RELATIVE REACTIVITIES OF 1,2-*trans*-SUGAR ACETATES[1]

By R. U. Lemieux and Carol Brice

ABSTRACT

The rates of exchange of the C1-acetoxy group of a variety of 1,2-*trans*-sugar acetates with acetate from stannic trichloride acetate labelled with carbon-14 were determined in chloroform containing stannic chloride. A correlation was found to exist between reactivity and configuration with the configuration at C3 playing a dominating role. The greater reactivity of the 2,3-*trans*-sugar compounds is attributed to steric inhibition to the formation of the resonance stabilized intermediate 1,2-cyclic carboxonium ion in the case of the 2,3-*cis*-compounds.

In view of the central role played by acetylated sugars, glycosides, and glycosyl halides in the field of synthetic carbohydrate chemistry, it is important that the chemical properties of these substances be well understood. It is especially important that information be gained on those factors which affect the reactivity of the C1 to aglycon group bond. Such data are not, however, readily obtained. The unstable anomers of most of the acetylated glycosyl halides are not suitable for study because of their extremely high reactivity (14, 22). On the other hand, the much more inert acetylated alkyl glycosides possess the undesirable property of undergoing reaction by way of very complex reaction routes (19). Both the anomeric forms of sugar acetates are usually sufficiently unreactive to allow purification and the results of studies on pentaacetates of glucose (15), galactose (14), and mannose (16) suggest that these substances undergo reaction at the anomeric center in a reasonably straightforward fashion. The sugar acetates therefore appeared more attractive for study than the closely related acetylated glycosides and glycosyl halides. In view of the evidence (14, 16, 18) that 1,2-*trans*-sugar acetates tend to undergo reaction at the anomeric center with participation of the C2-acetoxy group, it appeared desirable to consider these compounds as a group. The behavior of the compounds could of course be studied under a wide variety of reaction conditions. It appeared to us that perhaps the reaction conditions least susceptible to complicating factors would be those developed by the authors (16) in which the rate of exchange—concurrent with anomerization—of acetate between the C1-acetoxy group of a sugar acetate and stannic trichloride acetate (labelled in the carboxyl group with carbon-14) is determined. The exchange technique (16) was applied to the four diastereoisomeric 1,2-*trans*-aldopentopyranose tetraacetates, five diastereoisomeric 1,2-*trans*-aldohexopyranose pentaacetates (glucose, mannose, galactose, altrose, and allose), and the 1,2-*trans*-acetates of 6-deoxyglucopyranose and D-glycero-D-guloheptopyranose. Data typical of the experimental results are plotted in Figs. 1, 2, 3, and 4.

A consideration of the data shows that the reaction followed the simple exponential law for exchange reactions (4) during the early stages. However,

[1]*Manuscript received March 13, 1956.*
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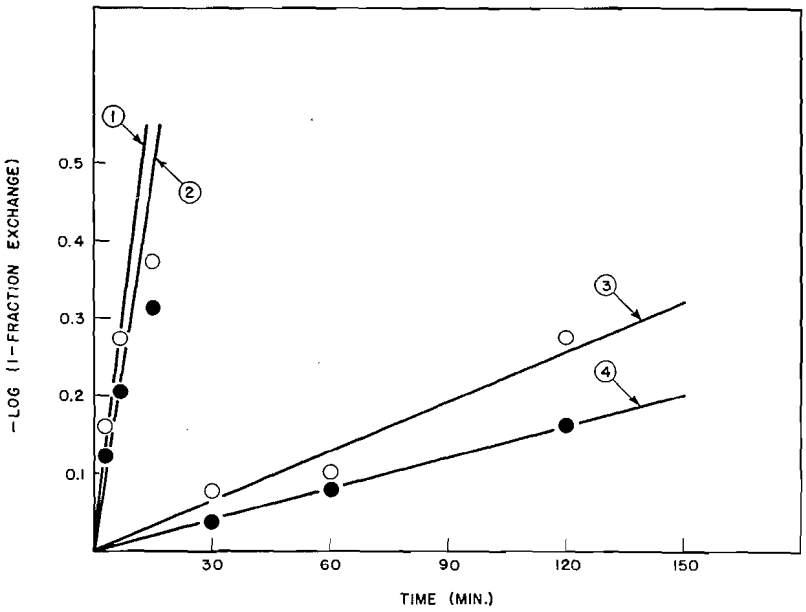

FIG. 1. Rates of exchange under the conditions given in Table I at 20° C.
Plot 1. β-D-xylopyranose tetraacetate—○
Plot 2. α-L-arabinopyranose tetraacetate—●
Plot 3. β-D-ribopyranose tetraacetate—○
Plot 4. α-D-lyxopyranose tetraacetate—●

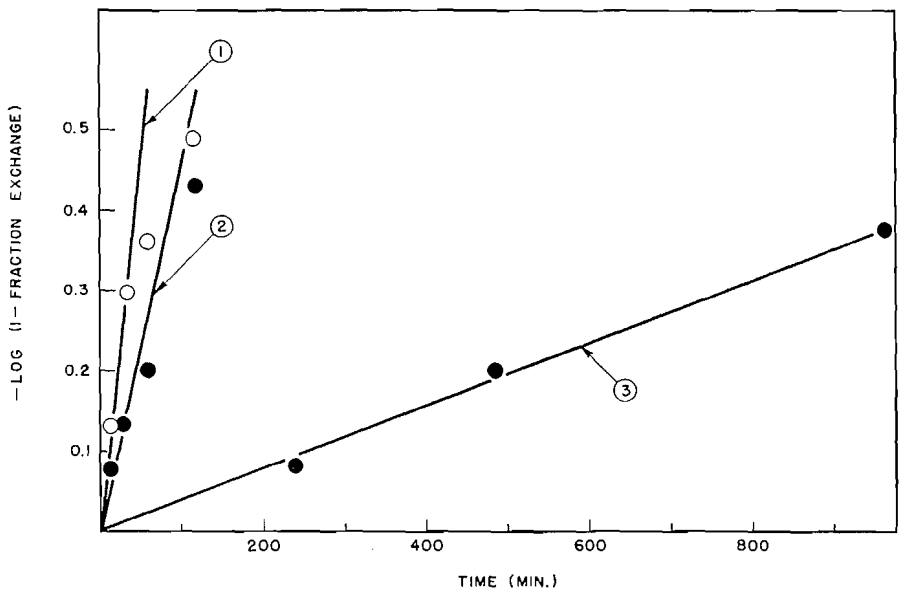

FIG. 2. Rates of exchange under the conditions given in Table I at 20° C.
Plot 1. α-D-altropyranose pentaacetate—○
Plot 2. β-D-glucopyranose pentaacetate—●
Plot 3. α-D-mannopyranose pentaacetate—●

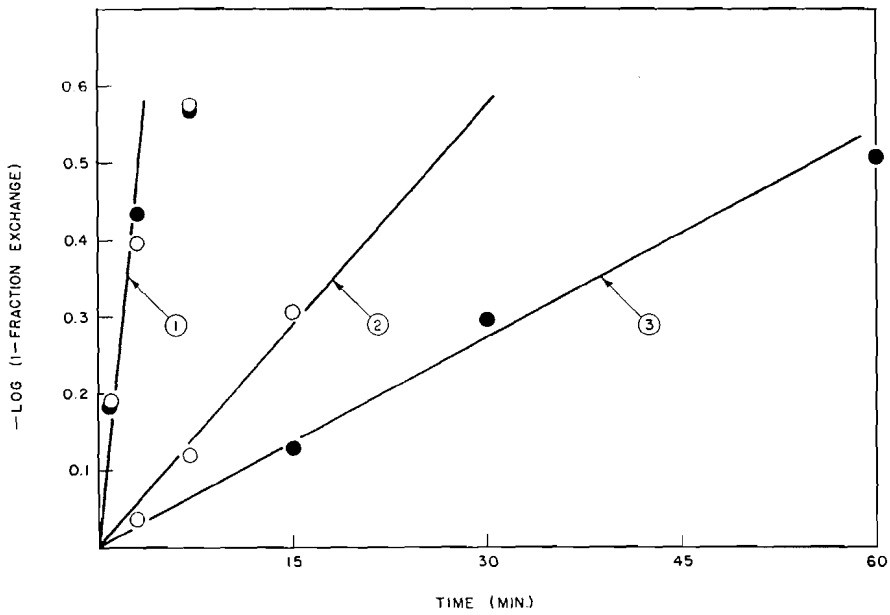

FIG. 3. Rates of exchange under the conditions given in Table I at 40° C.
Plot 1. β-D-xylopyranose tetraacetate—○ and
α-L-arabinopyranose tetraacetate—●
Plot 2. β-D-ribopyranose tetraacetate—○
Plot 3. α-D-lyxopyranose tetraacetate—●

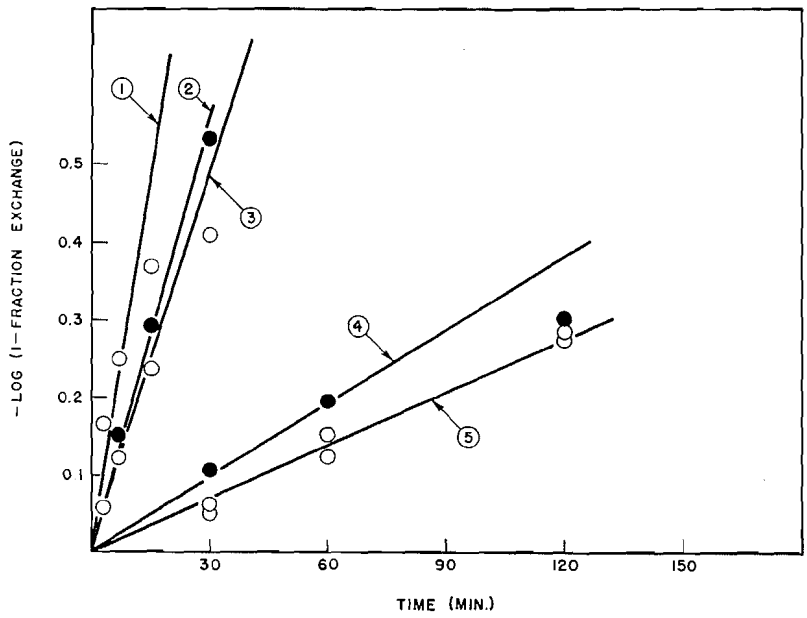

FIG. 4. Rates of exchange under the conditions given in Table I at 40° C.
Plot 1. α-D-altropyranose pentaacetate—○
Plot 2. β-D-glucopyranose pentaacetate—●
Plot 3. β-D-galactopyranose pentaacetate—○
Plot 4. β-D-allopyranose pentaacetate—●
Plot 5. α-D-mannopyranose pentaacetate—○

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it is seen that in several cases there was strong deviation after about 60% exchange. This is the situation to be expected under conditions where the exchange reaction is accompanied by a reaction which leads to replacement of the C1-acetoxy group. Pacsu (21) has shown that the reaction of a sugar acetate with stannic chloride can yield acetochlorosugar and, in fact, in the present experiments the reaction products isolated after the prolonged reaction times invariably contained chlorine. However, the results indicate clearly that in all cases the formation of acetochlorosugar was much slower than the exchange. Consequently, it can be assumed that the slope of the line (log(1−fraction exchange) versus time) drawn through the points obtained in the early stages of the reaction is proportional to the rate of exchange and can serve as a measure of the reactivity of the sugar acetate under the conditions used. Since the initial conditions were the same for each sugar acetate, a comparison of the slopes provides a measure of the relative reactivities of the sugar acetates. The relative reactivities listed in Table I were calculated setting the

TABLE I

RELATIVE RATES OF EXCHANGE OF ACETATE BETWEEN 1,2-*trans*-SUGAR ACETATES AND STANNIC TRICHLORIDE ACETATE

The sugar acetate, 1 mM., was dissolved at zero time in 20 ml. of chloroform containing 1 mM. of stannic chloride and 1 mM. of stannic trichloride acetate labelled in the carboxyl group with carbon-14 (16)

Fully acetylated pyranose form	Temperature of reaction: 20° C. Relative rates Found	20° C. Calc.[a]	40° C. Relative rates Found	40° C. Calc.[b]	Temperature coefficient, $R_{40°}/R_{20°}$
β-D-Xylose	100[c]	100	100[c]	102	4.0
α-L-Arabinose	81	96	100	95	4.9
β-D-Ribose	5.3	7	11.9	13	9.0
α-D-Lyxose	3.3	3	5.7	6	7.0
α-D-Altrose	23	32	21	19	3.6
β-D-Glucose	11.8	12.5	11.9	12.8	4.0
β-D-Galactose	8.7	12	10.6	12	4.9
β-D-Allose	—	—	2.00	1.6	—
α-D-Mannose	0.98	1.0	1.43	1.2	5.9
β-D-6-Deoxyglucose	—	—	7.8	—	—
D-Glycero-β-D-guloheptose	0.032	—	—	—	—

[a] *Using equation [1].*
[b] *Using equation [2].*
[c] *Arbitrarily set at 100.*

reactivity of β-D-xylopyranose tetraacetate at 100 for both the runs made at 20° C. and at 40° C. The increase in reactivity caused by the increase in temperature is shown.

No difficulty was experienced in reproducing the values listed in Table I within the limits of the rather large experimental error. This is seen, for example, by the plots in Fig. 4 of two runs for α-D-mannopyranose pentaacetate. To ensure against any difficulties in reproduction which are often reported for reactions catalyzed by Lewis acids such as stannic chloride, several of the sugar acetates were always run together using the same stock solution of stannic chloride and stannic trichloride acetate. Furthermore, a

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sugar acetate was used as a control by including it in each batch of runs. The reactivity of the compound used as control never varied significantly from one run to the next.

The results allow broad conclusions on the effect of configuration on the reactivity of a 1,2-*trans*-sugar acetate which are in no way obscured by the uncertainties in the experimental data. Examination of the content of Table II

TABLE II

THE EFFECT OF CONFIGURATION ON THE REACTIVITY OF A 1,2-*trans*-SUGAR ACETATE

	Ratio of reactivities[a]	
	20° C.	40° C.
1. 1,3-*cis*-Compound/1,3-*trans*-Epimer		
(*a*) xylo/ribo	19	8
(*b*) arabo/lyxo	25	18
(*c*) gluco/allo	—	6
(*d*) altro/manno	25	15
2. 1,4-*trans*-Compound/1,4-*cis*-Epimer		
(*a*) xylo/arabo	1.2	1.0
(*b*) ribo/lyxo	1.6	2.1
(*c*) gluco/galacto	1.4	1.1
3. 1,5-*trans*-Compound/1,5-*cis*-Epimer		
(*a*) altro/galacto	2.6	2.0
4. Introduction of CH_2OAc at C5 of a pentose acetate in *cis*-relationship to the C1-acetoxy group		
(*a*) xylo/gluco	8.5	8.4
(*b*) ribo/allo	—	6.0
(*c*) arabo/galacto	9.3	9.4
5. Introduction of CH_2OAc at C5 of a pentose acetate in *trans*-relationship to the C1-acetoxy group		
(*a*) arabo/altro	3.5	4.8
(*b*) lyxo/manno	3.4	4.0

[a]*The reactivities are listed in Table I.*

shows that epimeric 1,2-*trans*-sugar acetates differ greatly in reactivity when the difference in configuration is at C3. In fact, it seems clear that for a group of diastereoisomeric 1,2-*trans*-sugar acetates, the configuration at C3 has the overriding influence on reactivity. The data indicate that the compounds differ little in reactivity when the epimerism is at C4. It is seen that a pentose acetate is considerably more reactive than the homomorphous hexose acetate, the introduction of a CH_2OAc group for hydrogen at C5 of a pentose causing an about eight-fold decrease in reactivity when introduced *cis* to the C1-acetoxy group and an about four-fold decrease when introduced in *trans*-relationship.

Before considering these matters in detail, it is of interest to note that it is possible to correlate within an impressive degree of accuracy the reactivities at a given temperature listed in Table I by means of simple mathematical expressions ([1] and [2]). These expressions were derived empirically by giving the symbols a, b, c, x, y, and z in formula I values of zero when they correspond to a hydrogen atom and values of one when they correspond to an acetoxy or

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CH_2OAc group and arriving at their coefficients by trial and error. The calculated reactivities at 20° C. listed in Table I were calculated from the expression

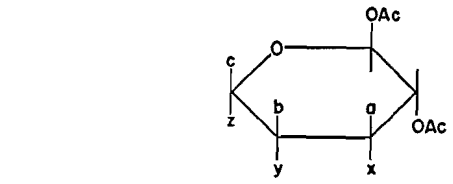
$$[1] \qquad R_{20^\circ} = \frac{95a+2x+b+5y}{7c+2z+1},$$

and the expression

$$[2] \qquad R_{40^\circ} = \frac{94a+5x+b+8y}{7c+4z+1}$$

was used at 40° C. It seems reasonable that these correlations between reactivity and configuration should exist since steric effects can be expected to play the dominating role in determining the *relative* reactivities of closely related diastereoisomeric compounds and the steric effects are determined by configuration.

Several attempts have been made recently (5, 6, 11) to correlate the reactivities of sugar derivatives in reactions at the anomeric center with the stabilities of the compounds as judged by conformational analysis. The present results have an important bearing on these speculations. It seems well established (16, 17) that the dissociation of the C1-acetoxy group of a 1,2-



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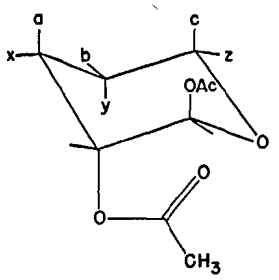

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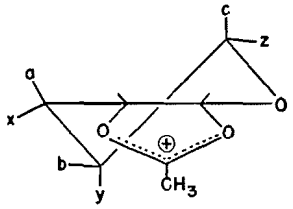

III

trans-sugar acetate proceeds primarily with *direct* participation of the C2-acetoxy group. Therefore, it can be expected that these compounds achieve the conformation of II before dissociation can begin since axial orientations for the leaving and participating groups should be the most favorable situation (24). Direct evidence has been obtained that this is the case in the dissociation of 1,2,3,4-tetra-*O*-acetyl-β-D-glucose by stannic chloride (15). Obviously, on the basis of these considerations one would not expect β-xylose tetraacetate to be the most reactive 1,2-*trans*-pentose tetraacetate if only the ground states of

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the molecules are considered since β-xylose tetraacetate in conformation II possesses all four acetoxy groups in axial orientations. The high reactivity of this compound can however be rationalized by a conformational analysis of the steric requirements for the formation of the intermediate 1,2-cyclic carboxonium ion III. The basis for depicting the ion in the particular conformation shown has been discussed by Lemieux and Cipera (18). The steric requirements for the ion III can be met, of course, with the pyranose ring in a boat conformation and it is noteworthy that a superficial rationalization of the present data can be based on the boat form which would possess the five-membered ring in "equatorial" orientation. However, this must be merely a coincidence since the direct formation of III in this conformation appears unlikely for a number of reasons which will become clearly apparent in the foregoing discussions.

Winstein and co-workers (23) have shown that the driving force for reaction provided by neighboring acetoxy group participation is related mainly to the heat of activation term in the transition-state-theory expression for specific rate of reaction and this result was related to resonance stabilization of the 1,2-cyclic-carboxonium-ion intermediate. The fact that any instability or stability factor in the intermediate ion is in all probability present to an important extent in the transition state is basic to these discussions.

Definite evidence has accumulated (16, 18) that, as expected from the work of Winstein and co-workers (23), the participation of the C2-acetoxy group in the dissociation of a 1,2-*trans*-sugar acetate can provide a powerful driving force for the reaction. The present results indicate that in all probability the strong influence of the configuration at C3 on the reactivity of these substances is mainly related to steric inhibition to achievement and to resonance stabilization of the ion by deformation of the planar five-membered ring structure when the C3-acetoxy group is in *cis*-relationship to the C2-substituent because of eclipsing of these groups in the half-chair conformation of III. The basis for this conclusion is readily seen from a consideration of the data for the pentose acetates. Although the results listed in Table I are subject to rather large experimental error, there can be no doubt that the reactions of the 2,3-*cis*-pentose acetates possess much higher temperature coefficients than do those of the 2,3-*trans*-diastereoisomers (Formulas IV–IX). In the case of the xylose (IV–V) and lyxose (VII–VIII) derivatives these coefficients correspond to energies of activations of roughly 13 and 18 kcal. per mole, respectively. Therefore, the heat of activation for the xylose derivative is about 5 kcal./mole less than for the lyxose compound. This observation is in accord with the above postulation that the higher reactivity of the xylose tetraacetate (IV–V) is related to steric inhibition to achievement of resonance stabilization in the ion (IX) derived from the lyxose compound (VII–VIII). Since Winstein and co-workers (23) have concluded that neighboring acetoxy group participation can lend a driving force for reaction of this order (4.6 kcal./mole at 25° C.), the results suggest strong steric inhibition to resonance in the ion IX. It will be seen below that the configuration at C4 in the ion IX also contributed to this condition.

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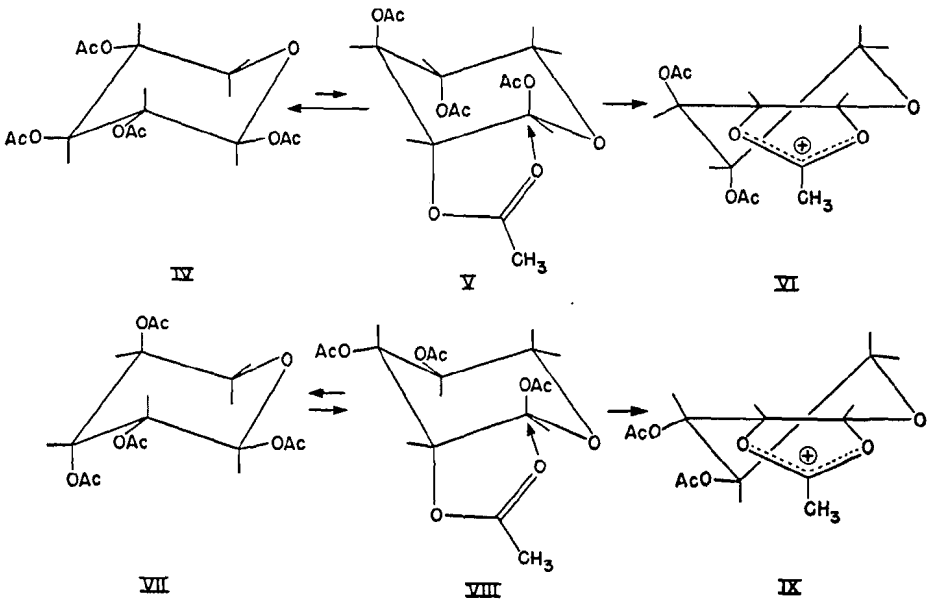

Since a difference in heat of activation of 5 kcal./mole would require a difference in reactivity by a factor of about 3000 and the xylose compound is only 30 times more reactive than the lyxose tetraacetate, it is evident that the entropy of activation for the former compound must be much greater (about nine entropy units) than the latter substance. This situation appears reasonable from a consideration of the substances in their ground states relative to the transition states. Since the xylose tetraacetate must exist almost entirely in the conformation IV while the structure VIII is highly probable for the lyxose tetraacetate, it follows that the lyxose derivative exists in a conformation which is much closer to that of the transition state than does the xylose compound. Therefore, it is reasonable that the probability for achievement of the transition state (entropy of activation) should be greater for the lyxose tetraacetate than for the xylose diastereoisomer.

The fact that the configuration at C3 plays a dominating role among the factors which determine the reactivity of 1,2-*trans*-sugar acetates therefore appears related to the more ready achievement and more effective resonance stabilization of the intermediate carboxonium ion (III) in the case of the 2,3-*trans*-compounds. Thus, the large coefficients for a in expressions [1] and [2] are understandable. This conclusion promises to be of practical value since it appears to provide a deepened understanding of the properties of related compounds. For example, the fact that β-D-xylopyranosyl chloride triacetate (22) appears to be more reactive than β-D-ribopyranosyl chloride triacetate (25) is no longer surprising. Lemieux and Cipera (18) have shown that the hydrolysis of an acetylated sugar (methyl 1,2-orthoacetate) catalyzed by acid in all probability proceeds by way of the 1,2-cyclic carboxonium ion (III). Therefore, the fact that 2,3-*cis*-mannose (methyl 1,2-orthoacetate) triacetate is more resistant to hydrolysis than the corresponding 2,3-*trans*-derivative of glucose

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(14) appears at least in part understandable. Also, Isbell and Frush (13) have found the course of the reaction of 2,3-*cis*-α-D-mannopyranosyl bromide tetraacetate with methanol in the presence of silver carbonate to be markedly temperature dependent and to yield substantial amounts of methyl β-D-mannopyranoside tetraacetate. This result clearly points to a steric hindrance to reaction with participation of the C2-acetoxy group which is increased by increased kinetic disturbance of the molecule.

The deactivation which results on the introduction of a CH_2OAc group for a hydrogen atom at C5 of a pentose acetate is reminiscent of the same result found in the hydrolysis of methyl glycopyranosides (12). The present discovery that the configuration of C5 in the case of the hexose acetates has only a twofold to threefold effect on reactivity was unexpected in view of the important role the CH_2OAc group has been predicted to play in determining the reactivity of related compounds (9). The fact that deactivation occurs for both the configurations of C5 could be taken as indication that the effect is mainly electronic in nature. However, we submit that the deactivations are produced mainly by steric factors. The deactivation brought about by a large substituent at *c* can be attributed to the instability of conformation II and to the interference by this substituent when in axial orientation with the coordination of the acid catalyst with the C1-acetoxy group. The deactivation caused by an increase in the bulk of the substituent at *z* can, on the other hand, be attributed to steric inhibition to achievement of the half-chair conformation (III) for the carboxonium ion, which results from the fact that in the conformation of III, the *z* and *b* substituents are very nearly in one plane. Angyal and Macdonald (1) have provided chemical evidence for the eclipsing of these *trans*-substituents in the half-chair conformation and this fact is clearly demonstrated by a molecular model (3). Furthermore, this view is supported by the surprising observation that the preferred configuration at C4 for reactivity is that which possesses the large substituent in axial orientation (*y*) both in II and III since this odd result can only be rationalized through the assumption that eclipsing of the substituents at *b* and *z* renders the half-chair conformation (III) unstable. It is to be noted in this respect that substituents at *y* and *c* introduce much less instability in the half-chair conformation (III) than in the chair form (II) since in III there are no opposing axial groups.

The above conclusions appear to be of practical use. This fact is illustrated by the following considerations. First of all, for D-glycero-β-D-guloheptopyranose hexaacetate to undergo dissociation of the C1-substituent with participation of the C2-acetoxy group, the large $-CHOAcCH_2OAc$ group must achieve axial orientation (*c*) and the C3-acetoxy group (*x*) must eclipse the 1,2-ring structure in the ion III. Thus, the relatively great unreactivity found for this substance is not surprising. Furthermore, the fact (10) that 1,2-*trans*-D-glycero-β-D-guloheptopyranosyl chloride pentaacetate reacts with inversion of the anomeric center to form acetylated methyl α-D-glycoside *in quantitative yield* under conditions which normally afford a 1,2-orthoacetate appears understandable at least to the extent that it is not surprising that the compound should react by way of a route other than the highly sterically hindered

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route involving C2-acetoxy group participation. It has been reported (7) that 1,2-*irans*-D-glycero-α-D-idoheptopyranosyl bromide reacts with extensive inversion of the anomeric center when treated with methanol and silver carbonate. It is not surprising that the reaction should tend not to involve participation of the C2-acetoxy group when it is realized that achievement of the ion III involves bringing the C4-acetoxy group and the large $-CHOAcCH_2OAc$ group into nearly eclipsed orientations.

In conclusion, it can be stated that work along the lines reported in this communication promises to yield a much deepened insight into the properties of certain sugar derivatives. Although the present results allow certain important conclusions, the rather large uncertainties in the experimental results do not allow as detailed a theoretical analysis as would be desirable. It is hoped that improved conditions for studying the relative reactivities of sugar acetates will be discovered. The method used by Lemieux, Brice, and Huber (17) promises to yield superior experimental data. Perhaps the most important contribution of the present work is the clear illustration of the dangers attendant in any attempt to rationalize reactivities through the consideration of the relative stabilities of the substances in their ground states while disregarding structures and stabilities of the transition states.

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The authors wish to express sincere thanks to Dr. A. C. Neish for the generous gift of the rare sugars and to Dr. Ludovic Ouellet for useful discussions.

EXPERIMENTAL

Except for the β-D-allose pentaacetate, the compounds were prepared by published methods (2, 8) and recrystallized to a high state of purity.

D-Allose, 1 gm., was heated on the steam bath for two hours with 1 gm. of sodium acetate and 15 ml. of acetic anhydride. The sirupy product, 1.90 gm., $[\alpha]_D$ −3.28° (chloroform) was isolated in the usual manner. Chromatography on Magnesol-Celite according to the procedure of McNeely, Binkley, and Wolfrom (20) readily afforded 0.61 gm. of crude crystalline material which was purified by recrystallization from ethanol. The compound, m.p. 97–100° C., $[\alpha]_D$ −14.6° (*c* 1.5, in chloroform), was assumed to possess the β-D-configuration on the basis of its rotation and the stable pyranose structure on the basis of the yield.

The technique used to determine the rates of exchange has already been reported in detail by Lemieux and Brice (16).

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NOTES

A LOW TEMPERATURE CELL FOR USE WITH THE CARY ULTRAVIOLET SPECTROPHOTOMETER[1]

By R. N. Jones and D. S. Keir

Several cells have been described for the measurement of ultraviolet absorption spectra at low temperatures (7, 11, 1, 8, 9, 4, 6). Most of these have been designed to handle samples cooled to rigid glasses at liquid nitrogen temperature, following the technique developed by Lewis and Lipkin (5). The cell to be described here is suitable for use with liquids at all temperatures down to −196°C. using liquid nitrogen as coolant. The essential feature is the design of the low temperature section as a single unit of fused quartz; this eliminates the strain problems that arise when adhesive seals are cooled or warmed too rapidly.

CONSTRUCTION OF THE CELL

The apparatus is shown diagrammatically in Fig. 1. It consists of a double walled inner cell (*A*) (4.3 cm. long × 0.9 cm. diameter), which is made of quartz with fused-on end windows. This is surrounded by an outer jacket (*B*) of Pyrex glass with quartz windows (*C*, C_1) attached with Benelite cement. The outer jacket can be evacuated through the stopcock (*D*). Simple evacuation provides sufficient thermal insulation to prevent frosting of the windows, so that silvering of the walls is unnecessary. This simplifies the observation of the inner cell during the cooling and measuring process. Access to the inner cell is provided through the narrow glass filling tube (*E*), which is attached to the quartz cell through a graded seal. The temperature in the cell is recorded by a fine thermocouple (not shown in the diagram) which passes down through (*E*). This thermocouple can be withdrawn immediately before the spectrum is measured, or it can be left in the beam and its obscuration allowed for in the solvent control measurement.

The cell is cooled through the quartz annular jacket (*F*), which is fused to it and extends from one end to a point 4 mm. from the opposite end, allowing clearance for the filling tube (*E*). The annular space is open to the center of the apparatus, to which it is attached through a graded seal that provides the main support. The annular space is filled with fine copper shot to increase the thermal capacity. The cell is demountable for cleaning and repair at the 50/60 standard ground joint which forms the upper part of the outer jacket. To cool the cell liquid nitrogen is dropped down the center of the apparatus at *G* from the reservoir. This is a Dewar flask provided with a glass needle valve (*H*) controlled by a screw passing down from the top.

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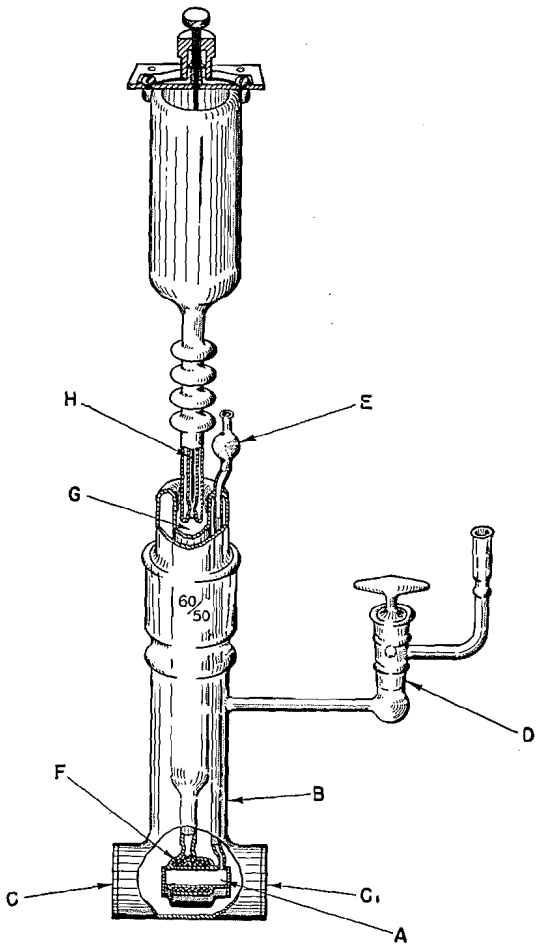

FIG. 1. Constructional details of the cell.

OPERATION

The apparatus is aligned in the upper cell compartment of the Cary spectrophotometer (sample beam) and two 1 cm. quartz cells of conventional type are placed in series in the lower compartment (reference beam). One of these cells is empty, to compensate for reflection losses at the outer quartz windows. In initial experiments the second cell was filled with the solvent used in the experimental cell, but later it was found more convenient to keep this cell filled with distilled water.

Before the experimental solution is measured, a control curve is first obtained. The cell is filled to the top of the filling tube (*E*) with the solvent, the thermocouple leads inserted, and liquid nitrogen dropped into the cooling chamber at a rate of about one drop per second until the temperature reads −80°C. The nitrogen flow is then reduced so that the temperature first levels off near −110°C. and then increases slowly to −100°C. The cell is held at

this temperature for 10–15 min. after which the solvent control spectrum is recorded. The spectrophotometer is housed in a room that can be darkened; the cell compartment is covered with a black cloth, and the actual measurement made with the room lights out and localized red illumination on the strip-chart recorder.

Provided the solvents are pure, these control curves show a steadily increasing absorption from about 0.1 optical density units at 4000 Å to 0.5 optical density units at 2300 Å; no measurements have been attempted at shorter wavelengths.

The cell is next allowed to warm to room temperature, this procedure being accelerated, if necessary, by opening the vacuum in the outer jacket. The solvent is replaced by the absorbing solution and the process repeated. To assure establishment of thermal equilibrium in the cell the spectrum can be rescanned several times until no further change is noted.

The molecular extinction coefficient corrected to room temperature (E_λ) is calculated from the equation

$$E_\lambda = \frac{1}{c.l} \cdot \frac{d_{22}}{d_{-100}} (OD_{soln} - OD_{solv}),$$

where c is the concentration of solute in moles per liter at room temperature (22°C.); d_{22} and d_{-100} the specific gravities of the solvent at 22° and −100°C. respectively; l the cell length in centimeters, which is determined optically from measurements of the absorption of standard potassium chromate solution (2); OD_{soln} the optical density of the solution as measured above, and OD_{solv} the correction term obtained from the solvent control measurement.

This cell has been used for solutions in ethanol, *n*-pentane, and isopentane. In the case of ethanol, care is needed to avoid excessive cooling, as on two occasions the cell has been fractured by solidification of the solvent. Hydrocarbon solvents were prepared by chromatographic adsorption on silica gel in a closed system protected from atmospheric moisture. Repeated experiments in which the same solutions were recooled showed variations in the optical density measurements in a range of ±0.05 *OD* units. These are larger than the variations reported by Potts (9) and by McConnell and Tunnicliff (6) in their measurements on glasses, but they are adequate for the purposes for which the cell was designed (10).

RESULTS

The spectra of naphthalene and anthracene obtained at room temperature and at −100° in ethanol solution with this cell are shown in Figs. 2 and 3. Other examples of the spectra of 1,2-benzanthracene derivatives in *n*-pentane solution will be published elsewhere (3, 10).

ACKNOWLEDGMENT

We are very grateful to Mr. G. Ensell for valuable assistance in the design and construction of this cell.

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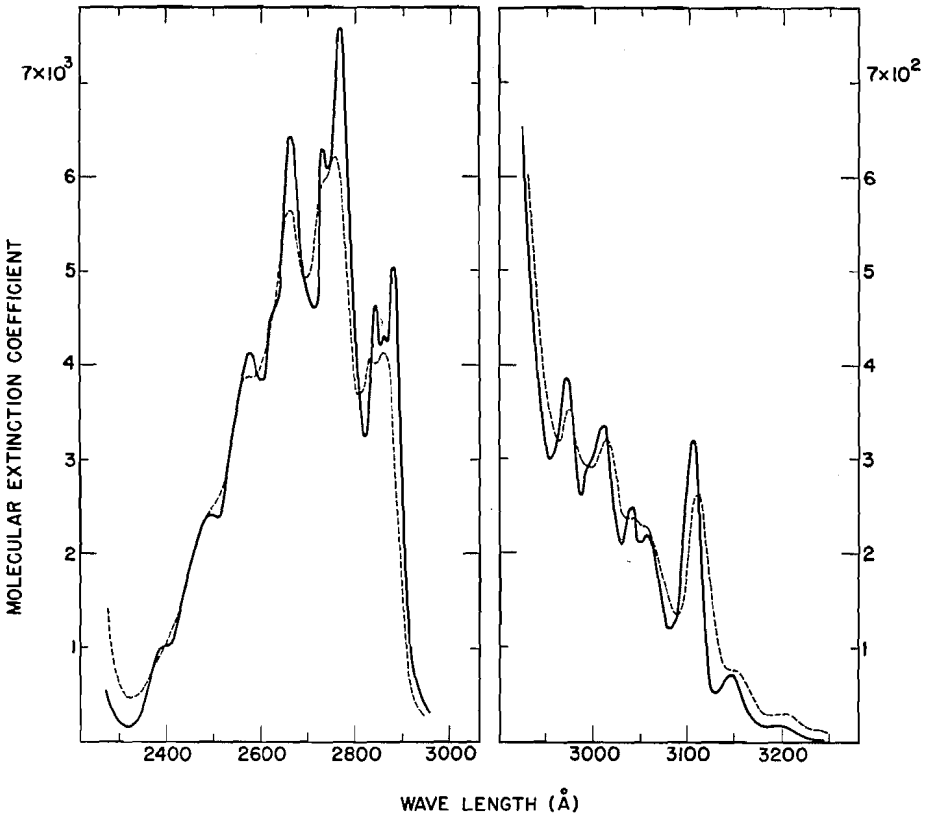

FIG. 2. Ultraviolet absorption spectrum of naphthalene in ethanol solution.
------ At 20°C. ——— At −100°C.

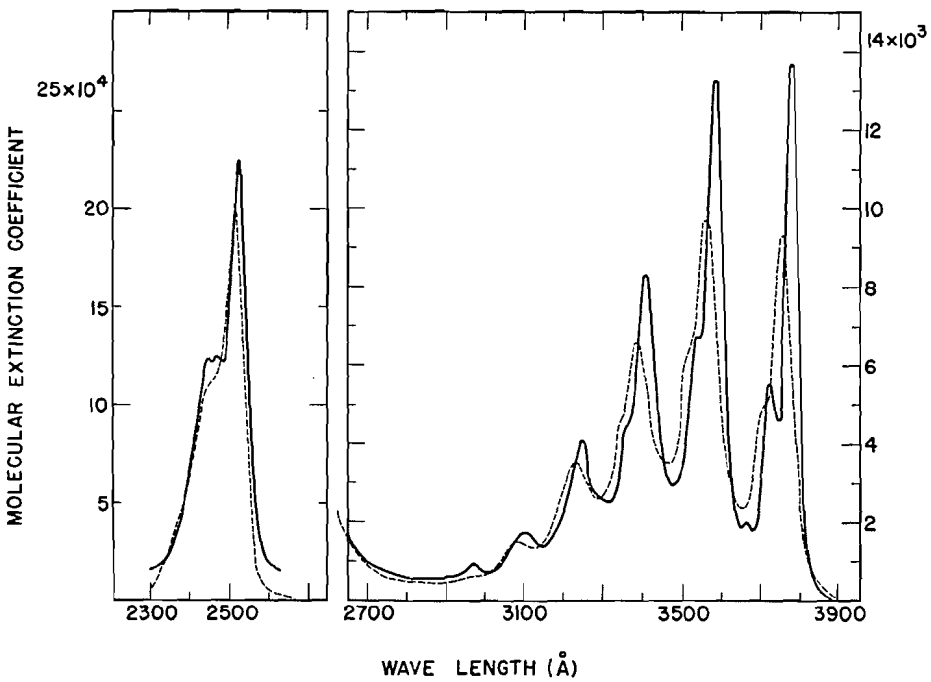

FIG. 3. Ultraviolet absorption spectrum of anthracene; experimental conditions as for Fig. 2.

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PHOTOLYSIS OF KETENE IN THE PRESENCE OF HYDROGEN

BY J. CHANMUGAM* AND MILTON BURTON

In a recent paper (3) on the photolysis of ketene in the presence of hydrogen, Gesser and Steacie† conclude that their results are such as to indicate that the reaction (1, 4)

$$CH_2 + H_2 \rightarrow CH_4 \qquad [3a]‡$$

occurs with low yield at room temperature and is unimportant at higher temperature, and that the reaction

$$2CH_3 \rightarrow C_2H_6 \qquad [5]$$

is the principal source of ethane.

The paper (2) to which Gesser and Steacie refer includes results on the photolysis of ketene in the presence of deuterium, of mixtures of hydrogen and deuterium, of acetone, and of CD_4, all as a function of temperature in the range 27° to 412°. Since the data are given in the form of extensive tables, some of the implications are not obviously apparent. One of the most important implications concerns the probability of ethane formation in ketene photolysis *via* reactions such as [5] in the presence of hydrogen or deuterium.

Fig. 1 summarizes the data for ethane yields from the photolysis of pure ketene and from the photolysis of ketene in the presence of deuterium or of an equimolar mixture of hydrogen and deuterium. The presence of hydrogen and deuterium causes a substantial increase in the yield of C_2H_6 and gives also $C_2H_4D_2$. In the presence of deuterium alone, $C_2H_4D_2$ but no C_2H_6 is produced. Significantly, no C_2H_5D is found. Our ability to recognize the "odd" mixed ethanes, if present, by the mass-spectrometric techniques employed is shown by our experiments (*not* included in Fig. 1) on the photolysis of ketene in the presence of CD_4. In the latter experiments, only C_2H_6, $C_2H_4D_2$, and $C_2H_2D_4$

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†*We are indebted to Drs. Steacie and Gesser for the opportunity to see this paper prior to publication.*
‡*Equation numbers are those of Gesser and Steacie.*

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Fig. 1 summarizes the data for ethane yields from the photolysis of pure ketene and from the photolysis of ketene in the presence of deuterium or of an equimolar mixture of hydrogen and deuterium. The presence of hydrogen and deuterium causes a substantial increase in the yield of C_2H_6 and gives also $C_2H_4D_2$. In the presence of deuterium alone, $C_2H_4D_2$ but no C_2H_6 is produced. Significantly, no C_2H_5D is found. Our ability to recognize the "odd" mixed ethanes, if present, by the mass-spectrometric techniques employed is shown by our experiments (*not* included in Fig. 1) on the photolysis of ketene in the presence of CD_4. In the latter experiments, only C_2H_6, $C_2H_4D_2$, and $C_2H_2D_4$

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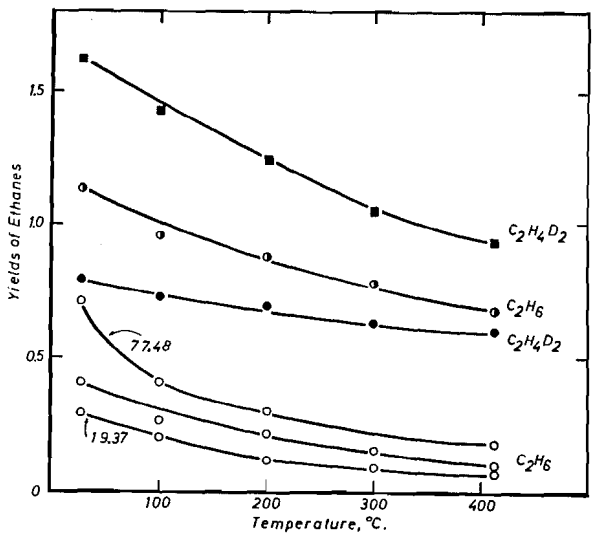

FIG. 1. Ethane yields in the photolysis of ketene, pure and in mixtures (2).
Initial concentrations are in units of 10^{-7} moles ml.$^{-1}$
Yields are in units of 10^{-8} moles ml.$^{-1}$
Initial concentrations: Ketene 38.74 unless otherwise indicated.
○: Pure ketene.
●◑: Mixture of H_2 and D_2, each 19.37.
■: D_2 38.74.

are found at room temperature but the odd mixed ethanes C_2H_5D, $C_2H_3D_3$, and C_2HD_5 (as well as C_2D_6) appear at the higher temperatures.

If C_2H_6 in our work with hydrogen and deuterium were produced by reaction [5], as postulated by Gesser and Steacie for their work with hydrogen, we should have expected also that the reactions

$$CH_2 + H_2 \rightarrow CH_3 + H, \qquad [3]$$

$$CH_2 + D_2 \rightarrow CH_2D + D \qquad [3']$$

might likewise yield ethane by the reaction

$$CH_3 + CH_2D \rightarrow C_2H_5D. \qquad [5']$$

The absence of C_2H_5D in our work has led us to the conclusion that ethane produced in the photolysis of ketene in the presence of hydrogen cannot to any significant degree result from a reaction such as [5].

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THERMAL NEUTRON CAPTURE CROSS SECTION OF Ce^{142} [1]

BY L. P. ROY[2] AND L. YAFFE

ABSTRACT

The cross section of Ce^{142} has been determined by the activation method and found to be 0.95 ± 0.05 barns relative to a value of $\sigma_{Co^{59}} = 36.3$ barns. Disintegration rates were determined by a 4π counter. The value obtained agrees with that of Katcoff *et al.* (1949) also obtained by the activation method but differs markedly from that of Pomerance (1952).*

INTRODUCTION

In the course of some related work (11) it became necessary to determine the capture cross section of Ce^{142} as accurately as possible. Bothe (1), by the activation method, had obtained a value of 1.1 barns relative to a value of 9 barns for the capture cross section σ of Ho^{165}. Using the most recent value of $\sigma_{Ho^{165}} = 64$ barns (7, 12), then $\sigma_{Ce^{142}} = 1.4$ barns according to Bothe. Katcoff *et al.* (5) obtained a value of 0.95 ± 0.18 barns by the activation method using uranium metal as a flux monitor. Pomerance (8) used the pile oscillator technique to obtain a value of 1.8 ± 0.2 barns for isotopically enriched Ce^{142}. He used $\sigma_{Au^{197}} = 95$ barns as a standard. Using the more recent value of 98.7 barns (2) Pomerance's value becomes 1.9 barns. The spread in these values was too great to be used in our work and large enough to warrant a redetermination of $\sigma_{Ce^{142}}$ by the activation method using improved techniques.

If naturally-occurring cerium were irradiated in a nuclear reactor the following first-order reactions would occur:

(1) $_{58}Ce^{136}$ (0.193% of natural cerium)

$$\xrightarrow{(n,\gamma)} {}_{58}Ce^{137} \xrightarrow[36\text{ hr.}]{\text{E.C.}} {}_{57}La^{137} \xrightarrow[>400\text{ yr.}]{\text{E.C.}} {}_{56}Ba^{137}\ (\text{stable})$$

[1]*Manuscript received March 23, 1956.*

Contribution from the Radiochemistry Laboratory, Department of Chemistry, McGill University, Montreal, with financial assistance from the National Research Council of Canada and the Atomic Energy Control Board.

[2]*Holder of a Shawinigan Chemical Scholarship (1952–53), a National Research Council Studentship (1953–54), and a Province of Quebec Bursary (1954–55). Present address: Atomic Energy of Canada Limited, Chalk River, Ont.*

*NOTE ADDED IN PROOF.—*Dr. Pomerance has been kind enough to inform us that his sample of enriched Ce^{142} showed a detectable amount (<1500 p.p.m.) of cadmium. His calculations show that, if the sample contained exactly 1500 p.p.m. of cadmium, his value for the cross section of Ce^{142} would be 1.0 ± 0.2 barns.

(2) $_{58}Ce^{138}$ (0.250% of natural cerium)
(n, γ)
$_{58}Ce^{139} \xrightarrow[140\text{ d.}]{\text{E.C.}} {}_{57}La^{139}$ (stable)

(3) $_{58}Ce^{140}$ (88.47% of natural cerium)
(n, γ)
$_{58}Ce^{141} \xrightarrow[32\text{ d.}]{\beta^-} {}_{59}Pr^{141}$ (stable)

(4) $_{58}Ce^{142}$ (11.07% of natural cerium)
(n, γ)
$_{58}Ce^{143} \xrightarrow[33\text{ hr.}]{\beta^-} {}_{59}Pr^{143} \xrightarrow[13.5\text{ d.}]{\beta^-} Nd^{143}$ (stable)

Owing to the multiplicity of radioactive cerium isotopes formed it is obviously very difficult to measure Ce^{143} directly. However it is possible to determine the activity of the Ce^{143} produced by separating and measuring its 13.5 day Pr^{143} daughter.

The differential equations involved are well known and it can be shown that the activity of Pr^{143} at any time t_1 after the irradiation is given by

$$[1] \qquad \lambda_2 C_{t_1} = \frac{\lambda_1\lambda_2}{\lambda_1-\lambda_2} B_T(e^{-\lambda_2 t_1} - e^{-\lambda_1 t_1}) + C_T\lambda_2 e^{-\lambda_2 t_1},$$

where B_T and C_T are the numbers of atoms of Ce^{143} and Pr^{143} respectively formed after a time of irradiation T and

$$[2] \qquad B_T = \frac{nvA\sigma_0}{\lambda_1}(1-e^{-\lambda_1 T})$$

and

$$[3] \qquad C_T = \frac{nvA\sigma_0}{\lambda_2}(1-e^{-\lambda_2 T})\frac{-nvA\sigma_0}{\lambda_1-\lambda_2}(e^{-\lambda_2 T} - e^{-\lambda_1 T}).$$

A is the number of atoms of Ce^{142} present during the irradiation in a neutron flux of nv neutrons/cm.^{2}/sec. and is assumed to be constant. σ_0, σ_1 and λ_1, λ_2 are cross sections and disintegration constants respectively, the subscripts 0, 1, 2 referring to Ce^{142}, Ce^{143}, and Pr^{143} respectively.

EXPERIMENTAL

Samples of spectroscopically pure cerium oxide were sealed into small quartz ampoules and irradiated in a position in the NRX Chalk River heavy water reactor where the neutron spectrum was predominantly thermal. With each sample was enclosed a piece of fine weighed cobalt wire which was used as a flux monitor.

After irradiation the cerium oxide was dissolved in boiling concentrated sulphuric acid to which a few drops of 30% hydrogen peroxide was added. Ten milligrams of praseodymium carrier was added and the rare earths precipitated by the cautious addition of ammonium hydroxide. The precipi-

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tate was dissolved in nitric acid and cerium separated by oxidation with solid potassium bromate and precipitation as ceric iodate. The supernatant, containing the praseodymium, was neutralized by cautious addition of concentrated sodium hydroxide which precipitated praseodymium hydroxide. The precipitate was dissolved, cerium carrier was added, and the entire cycle of cerium removal and praseodymium precipitation was repeated six or seven times. The final precipitate of praseodymium hydroxide was dissolved in 1 ml. of 6 *N* hydrochloric acid and made up to standard volume. The absolute disintegration rate was determined by the use of a 4π counter as described by Pate and Yaffe (6).

The cobalt wire monitor was dissolved in 1 ml. aqua regia, the solution made to standard volume, and its activity determined in a similar manner.

The chemical yield of the praseodymium was determined by precipitating it from the master solution as praseodymium oxalate and drying it to $Pr_2(C_2O_4)_3 \cdot 9H_2O$.

RESULTS AND DISCUSSION

The Pr^{143} was identified by its half-life. A typical decay curve is shown in Fig. 1. Values obtained from this and other samples which were followed

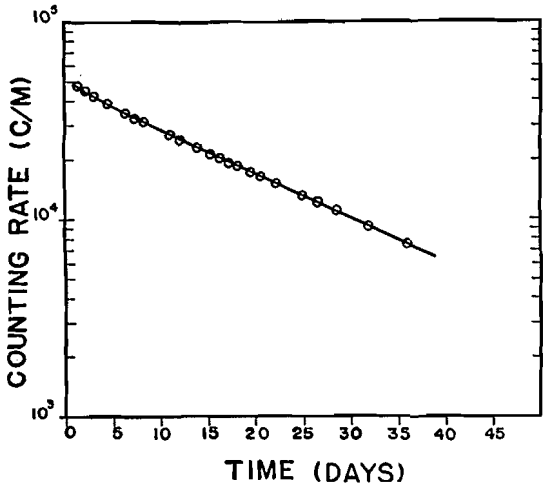

FIG. 1. Decay curve of Pr^{143}.

for about three half-lives ranged between 13.5 and 13.7 days. As can be seen from the previous discussion the only activity which could interfere from the cerium irradiation would be La^{137} which would not be separated from the praseodymium by the chemical procedures employed. A simple calculation shows that, owing to its long half-life, the La^{137} contribution to the activity will be negligible. Freedom from other rare earth radioactive impurities is attested to by the fact that the half-life obtained is very close to the currently accepted value (3, 4, 9, 10).

Table I shows the flux values obtained from the cobalt monitor. $\sigma_{Co^{59}}$ was taken as 36.3 (13) after correction for the more recent value of $\sigma_{Au^{197}} = 98.7$ barns (2).

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TABLE I

NEUTRON FLUX VALUES OBTAINED FROM COBALT MONITOR

Sample No.	Co^{59} atoms, $\times 10^{-19}$	Time, sec. $\times 10^{-4}$	Co^{60}, dis./sec. $\times 10^{-5}$	Calc. flux, n./cm.^{2}/sec. $\times 10^{-12}$
1	1.17	3.70	6.1	9.24
2	1.17	7.19	3.6	2.80

In Table II are shown the values of the cross section of Ce^{142} as calculated by means of equation [1].

TABLE II

VALUES OF CROSS SECTION OF Ce^{142} OBTAINED

Sample No.	A, Ce^{142} atoms $\times 10^{-18}$	t_1, sec. $\times 10^{-5}$	$\lambda_3 C_{t_1}$, dis./sec. $\times 10^{-5}$	σ_0, barns
1*a*	8.24	1.214	8.44	0.945
1*b*	8.24	1.214	8.46	0.948
1*c*	8.24	1.214	8.44	0.945
2*a*	9.31	2.760	7.98	0.965
2*b*	9.31	2.760	7.94	0.961
2*c*	9.31	2.760	7.98	0.965

An average value of 0.95 ± 0.05 barns was obtained, in excellent agreement with the value of Katcoff *et al.* (5). The error quoted is five times the standard deviation obtained and certainly takes into account systematic errors. It is difficult to understand the higher value obtained by Pomerance.* Two possibilities occur to us. First, the cerium sample used by him might have contained small amounts of high neutron-absorbing rare earth impurities. Secondly Ce^{143} may form a short-lived isomer. The cross section for its formation would not be detected by our technique but would be measured by the pile oscillator method.

ACKNOWLEDGMENTS

One of us (L. P. R.) wishes to express his gratitude to Shawinigan Chemicals Limited, the National Research Council of Canada, and the Province of Quebec for financial assistance during the course of this and allied researches.

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See footnote to Abstract.

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GRAFT COPOLYMERS OF STYRENE AND METHYL METHACRYLATE

PART II: VISCOSITY BEHAVIOR[1,2]

By M. H. Jones

ABSTRACT

A study of the viscosity behavior of the graft copolymers described in Part I has been made with dilute solutions in benzene at 25°C. Although the slope constants of the Huggins equation increase with the frequency of branching when measurements are made in a capillary viscometer under 'free fall' conditions, this is shown to be attributable to the dependence of viscosity on shear gradient. At a constant shear rate, the Huggins k' values approximate to those of linear polymers. It is suggested that the marked increase in viscosity observed with decreasing shear rate for the graft copolymers is due to molecular entanglement.

INTRODUCTION

Although the viscosity behavior of dilute polymer solutions has been studied actively for a number of years, most of the experimental evidence is concerned with polymers which are essentially linear in structure and little is known of the influence of branching.

Through a modification of the Stokes equation to take into consideration interactions between solvent and polymer molecules, Huggins (7) has derived the expression

$$\eta_{sp}/C = [\eta]+k'[\eta]^2C+k''[\eta]^3C^2+ \ldots$$

relating the reduced viscosity to the concentration of the solution. For sufficiently dilute solutions, only the first two terms of the series are significant. The interaction coefficient, k', is considered to be a constant for a given solvent–polymer system and, in general, is independent of molecular weight. This is similar to the empirical equation of Schulz and Blaschke (12). Increases in the slope constant for high molecular weight fractions from polymerization carried to high conversions, where the rate of transfer to polymer resulting in the formation of branched molecules is more significant, have been attributed to branching (4, 5, 11). A similar explanation has been given to observed increases in k' for soluble fractions of styrene – divinyl benzene copolymers (10, 17) where branching occurs through the unreacted double bonds of the diolefinic units in the polymer chain. Theoretical calculations (14) have supported this contention. However, the results of Thurmond and Zimm (16) show no detectable difference in the slope constant of the Huggins equation between fractions of a styrene – divinyl benzene copolymer and a polystyrene prepared under identical conditions. Decreases in the exponent of the Houwink viscosity – molecular weight relationship for high conversion polybutadienes (8) and soluble crosslinked polystyrenes (8, 16) have also been attributed to branching.

[1]*Manuscript received March 21, 1956.*
Contribution from the Department of Chemistry, Ontario Research Foundation, Toronto 5, Ontario.
[2]*Presented in part at the 6th Canadian High Polymer Forum held at St. Catharines, Ontario, April 14–15, 1955.*

The series of well-characterized branched molecules described in Part I provide a means of studying some of these effects and observing their change with progressive increments of branching.

EXPERIMENTAL

Materials

Samples of homopolymers and random copolymers of styrene and methyl methacrylate were prepared by bulk polymerization using α,α'-azo-bis-isobutyronitrile as initiator. The preparative conditions are recorded in Table I. Polymerizations were limited to small conversions at comparatively

TABLE I

LINEAR POLYMERS AND COPOLYMERS OF STYRENE AND METHYL METHACRYLATE

Polymer	Poly^n Temp. (°C.)	[Initiator] (gm. l.$^{-1}$)	Mole fraction MMA	% Poly^n	% PMMA in copolymer
PS 1	70			12.5	
PS 2	45	0.98		4.8	
PMMA 1	60	1.87		9.3	
PMMA 2	60	0.28		7.4	
Cop 1	60	0.30	0.811	7.1	71
Cop 2	60	0.30	0.682	6.0	60
Cop 3	60	0.30	0.508	5.2	50
Cop 4	60	0.093	0.682	5.2	58

low temperatures; these conditions are such that branching may be considered negligible. The compositions of the copolymers were determined by infrared analysis. The method of synthesis of the graft copolymers has been described in detail in Part I.

Viscosity Measurements

Viscosity measurements were made in benzene solution at 25.0°C. ±0.005°C. using Ubbelohde and Ostwald type viscometers. A large bulb was incorporated in the Ubbelohde viscometer to permit dilution of the solution *in situ*. The Ostwald viscometer was similar to that used by Flory and his co-workers (6) and was designed to study the influence of shear rate on viscosity in the range encountered with the Ubbelohde viscometer. Kinetic energy corrections were calculated from the dimensions of the viscometers using the Wilberforce modification of the Poiseuille equation (1), i.e.

$$\eta = \frac{\pi r^4 hg\rho t}{8lv} - \frac{m\rho v}{8\pi lt}$$

or

$$\eta = A\rho t - \frac{B\rho}{t}.$$

A value of 1.1 (1) was chosen for the constant m and the corrections were applied to the flow times. Hence the corrected flow time

$$t^* = t - \frac{B}{At}.$$

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For the Ubbelohde and Ostwald instruments, the maximum kinetic energy corrections for the solvent were 0.9% and 0.5% respectively. As these are small, the arbitrary choice of a value for the empirical constant, m, was considered justifiable. Flow times were determined with a stop watch graduated in 1/10 sec. intervals and the reproducibility of successive readings was better than $\pm 0.1\%$. The dimensions of the two viscometers are given in Table II together with the corrected flow times for the solvent.

TABLE II

VISCOMETER CONSTANTS

Viscometer	v (cc.)	r (cm.)	l (cm.)	t^* (sec.)
Ubbelohde	2.20	0.0230	13.3	115.1
Ostwald: Upper bulb	2.37	0.0217	19.6	145.9†
Lower bulb	2.74	0.0217	19.6	222.3†

†*For solvent volume of 10.01 cc.*

Solution viscosities at different shear rates for a given polymer concentration were obtained by adding known volumes of the solution to the Ostwald viscometer. The maximum rates of shear, G, were derived from the expression

$$G = rhg\rho/2l\eta\eta_r$$

where η is the viscosity of the solvent and η_r the relative viscosity of the solution. The hydrostatic head, h, of the liquid column in the viscometer was taken as the arithmetic mean of the maximum and minimum heights. Although this differs from the true mean as calculated by a formula of the Meissner type (1), the maximum difference for the present viscometer was less than 1.5%.

Polymer solutions were prepared by shaking known weights of polymer with the solvent for 18 hr. to ensure complete solution. The solutions were filtered through sintered glass disks of medium porosity before transference to the viscometer. The usual precautions were taken to avoid contamination of the viscometers and solutions with dust particles. In general, reduced viscosities were determined at four or more concentrations in the range 0.05–0.40 gm./100 cc. and the parameters of the Huggins equation obtained by the least squares method of calculation.

RESULTS AND DISCUSSION

The parameters of the Huggins equation for the series of graft copolymers determined with the Ubbelohde viscometer under 'free fall' conditions are given in Table III. Similar data on the linear polystyrenes, polymethyl methacrylates, and random copolymers are included for comparison. Usually duplicate determinations were made and the slope constants agreed within 0.02 unit and the intrinsic viscosities within 1%.

The k' values for the linear polymers are constant at approximately 0.35. Even with small amounts of branching, i.e. one to two branches per molecule

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TABLE III

HUGGINS PARAMETERS FOR LINEAR AND GRAFT COPOLYMERS—VARIABLE SHEAR GRADIENT

Polymer	$\bar{P}_n$ (backbone)	$\bar{P}_n$ (branches)	Average no. branches per molecule	$[\eta]_{25°C.}$ (dl. gm.$^{-1}$)	k'
A1	2500	4500	1.2	3.26	0.40_5
A2	2500	1500	1.5	1.85	0.38_5
D1	3100	2300	2.6	3.10	0.54_0
D2	3100	1700	3.4	3.10	0.58_7
D3	3100	1600	3.0	3.17	0.61_3
D4	3100	1300	3.3	2.62	0.56_8
E1	3800	1500	1.8	2.99	0.43_1
E2	3800	1500	3.2	3.43	0.54_2
E3	3800	1800	3.9	3.66	0.63_4
E4	3800	1900	5.9	3.99	0.78_0
PS 1				3.16	0.33_5
PS 2				1.73	0.35_8
PMMA 1				1.84	0.35_5
PMMA 2				2.66	0.32_4
Cop 1				1.84	0.35_3
Cop 2				1.66	0.36_6
Cop 3				1.57	0.34_9
Cop 4				2.53	0.34_2

(Polymers A1, A2, and E1) there appears to be a significant increase in k' and, with more highly branched structures, the effect is pronounced. The progressive increase in slope constant with frequency of branching is most clearly demonstrated in the series E1–E4 where the variation in chain length is small compared to the increase in the number of branches. The reduced viscosity – concentration curves for these polymers are illustrated in Fig. 1. The broken lines indicate the slopes that would be obtained at the pertinent intrinsic viscosities for a k' value of 0.35. Although these results were obtained with the same viscometer and consequently at a constant shear stress, the reduced viscosities at each concentration during dilution are measured at progressively increasing shear gradients since these are an inverse function of the solution viscosity. In general, the shear gradients for a viscosity plot varied in the range 500–1500 sec.$^{-1}$.

Studies of the influence of molecular weight and solvent on the shear dependence of viscosity for neutral polymers have been reported by several authors (3, 6, 9, 13). Their results indicate that shear effects may just become significant at molecular weights of the same order as those of the present series of polymers and an investigation of the influence of shear rate was made to determine the magnitude of the effect. Although the range of shear gradients covered was small, a considerable difference in behavior was observed between the linear and branched molecules. Solutions of the polystyrene, polymethyl methacrylate, and the random copolymers, which were believed to have essentially no branching, behaved as Newtonian liquids (Figs. 2 and 3). The graft copolymers showed a marked dependence of viscosity

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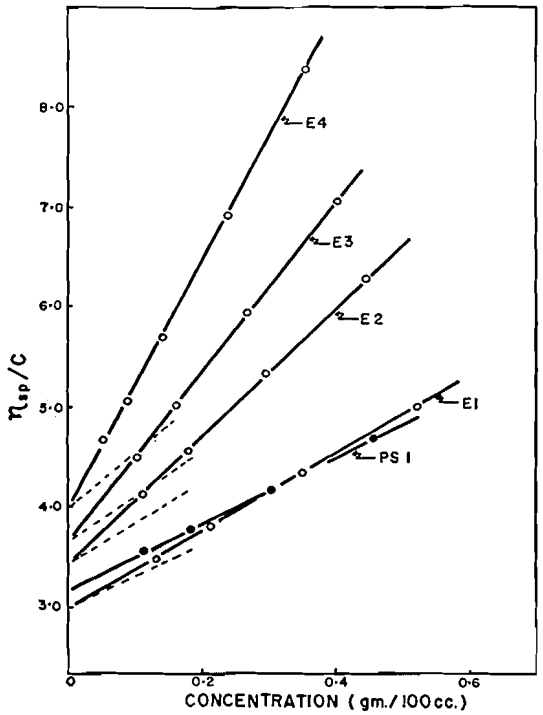

FIG. 1. Reduced viscosity versus concentration plots for graft copolymers E1–E4 with Ubbelohde viscometer.

on shear rate and this was clearly evident for samples having viscosities, and presumably molecular weights, similar to the linear polymers. Reduced viscosity – shear plots for the graft copolymers with the greatest difference in intrinsic viscosity are shown in Figs. 4 and 5. The curvature of the plots precludes the usual practice of extrapolating to zero shear gradient to obtain reduced viscosities that are independent of shear effects, and values for each concentration were taken from the curves at an arbitrary shear rate of 500 sec.$^{-1}$. Huggins plots of these values for two of the graft copolymers (E3 and E4) are illustrated in Fig. 6 together with the curves obtained under 'free fall' conditions with the same viscometer. For the polymer E3 the curves have been displaced downwards 0.5 unit in the ordinate scale for clarity. The values of the Huggins parameters for these two polymers and for a linear polystyrene and polymethyl methacrylate are recorded in Table IV. The significant result is that the slope constants for the graft copolymers, when measured at a constant shear rate, decrease to approximately the value obtained for polymers having a linear structure. This, again, emphasizes the necessity of determining shear dependence in capillary viscometry of high polymer solutions and demonstrates the fact that non-Newtonian behavior may appear as a unique viscosity–concentration effect in a relationship of the Huggins type when results are obtained under 'free fall' conditions. It is obvious that the increases in slope constant for the graft copolymers obtained with the

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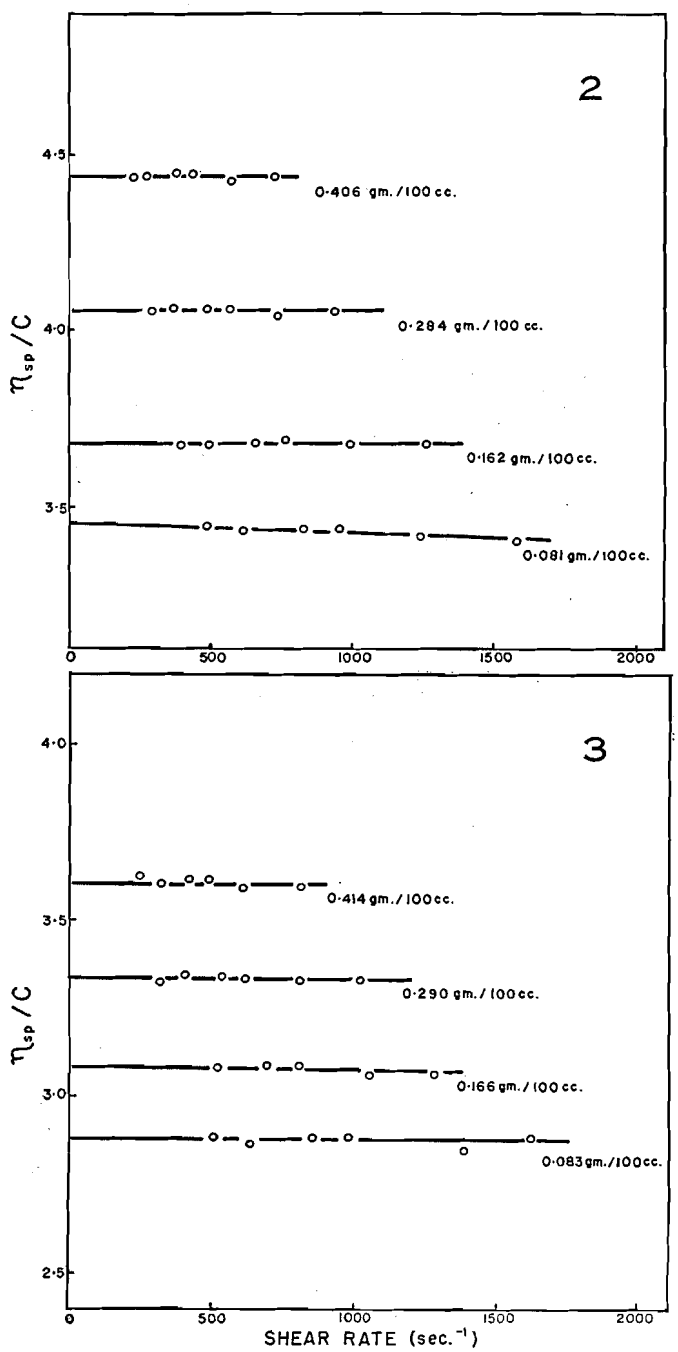

FIG. 2. Reduced viscosity versus shear rate plots for various concentrations of polymer PS 1.

FIG. 3. Reduced viscosity versus shear rate plots for various concentrations of polymer PMMA 2.

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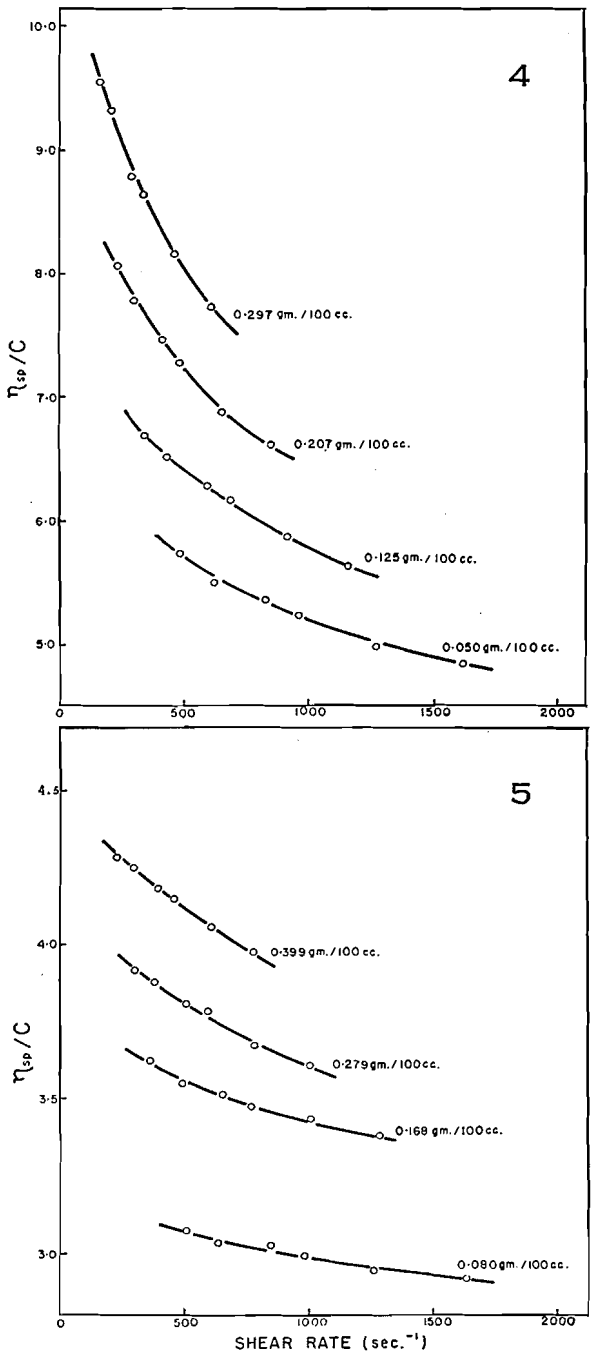

FIG. 4. Reduced viscosity versus shear rate plots for various concentrations of polymer E4.
FIG. 5. Reduced viscosity versus shear rate plots for various concentrations of polymer D4.

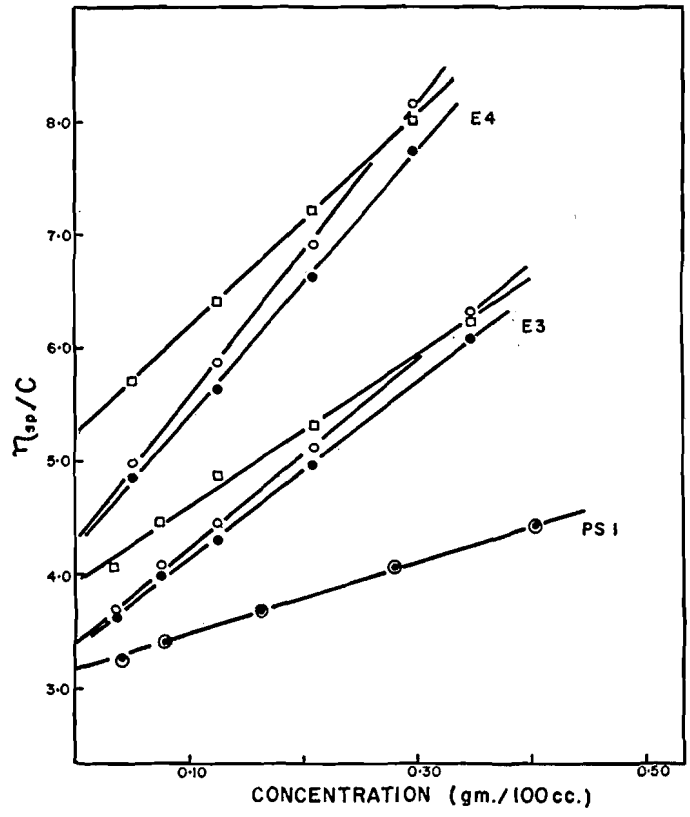

FIG. 6. Reduced viscosity versus concentration plots for graft copolymers E3 and E4 with Ostwald viscometer. Ostwald upper bulb—'free fall', -●-; Ostwald lower bulb—'free fall', -○-; Ostwald, constant G = 500 sec.$^{-1}$, -□-.

Ubbelohde viscometer (Table II) are fortuitous. Although the data on the shear dependence of viscosity are limited, slope constants have also been determined at constant shear rates of 250, 750, and 1000 sec.$^{-1}$ where errors due to extrapolation should not be too serious. The values obtained for the polymer E3 are, respectively 0.37, 0.34, and 0.34, and for the polymer E4, 0.39, 0.33, and 0.32. Although there appears to be a slight trend to increasing values of k' with decrease in shear rate, the variation is probably within the experimental accuracy.

It is to be expected that deviations from Newtonian behavior will be determined by the ease of deformation and orientation of the molecules in solution and, consequently, will be related to the molecular weight and 'goodness' of the solvent since these factors govern the extension and softness of the expanded coil. However, it must be assumed that branched molecules, with their greater density of packing, will be less subject to deformation under flow than linear molecules but the observations show that the latter are independent of shear rate. Probably the explanation lies in the greater probability of molecular entanglement with the branched polymers because of the increased number of

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TABLE IV

INFLUENCE OF SHEAR RATE ON HUGGINS PARAMETERS FOR LINEAR AND GRAFT COPOLYMERS

Viscometer	Shear rate (sec.$^{-1}$)	$[\eta]_{25°C.}$	k'
Polymer E3			
Ubbelohde	520–1380	3.66	0.63_4
Ostwald: Upper bulb	610–1750	3.84	0.53_3
Lower bulb	470–1380	3.89	0.55_5
	500	4.42	0.35_0
Polymer E4			
Ubbelohde	510–1630	3.99	0.78_0
Ostwald: Upper bulb	610–1620	4.21	0.66_0
Lower bulb	460–1270	4.28	0.70_3
	500	5.25	0.34_0
Polymer PS 1			
Ubbelohde	760–1440	3.16	0.33_5
Ostwald: Upper bulb	720–1780	3.13	0.33_3
Lower bulb	570–1390	3.16	0.31_3
	500	3.20	0.29_3
Polymer PMMA 2			
Ubbelohde	810–1550	2.66	0.32_4
Ostwald: Upper bulb	810–1620	2.71	0.28_8
Lower bulb	640–1280	2.68	0.31_2
	500	2.71	0.29_2

free chain ends. It must be remembered that for polymers in the present molecular weight range, the volume occupied by a single molecule is such that the concentrations employed for viscosity measurements are similar to the requirement for a system of close-packed spheres. From light scattering data (2), it has been estimated that the diameter of the sphere occupied by a polystyrene molecule of molecular weight 10^6 in benzene is approximately 1000 Å and this condition would be equivalent to a concentration of 0.24 gm./100 cc. Thus, for most of the solutions used, the molecules are in close proximity providing a greater concentration of aggregates (15). A combination of factors, such as orientation and deformation of loosely connected coils, may then contribute to the shear dependence.

For the Ubbelohde viscometer and the upper bulb of the Ostwald viscometer, with a solution volume of 10.01 cc., the constant factor in the shear rate expression, i.e. $rhg\rho/2l\eta$, differs by only 0.5%. Thus, the slope constants determined at 'free fall' with these two systems should be practically identical. The fact that the values obtained for the graft copolymers with the Ostwald instrument are lower may be attributable to a greater degree of molecular disentanglement. The differences for the linear polymers are within the experimental accuracy. For the Ubbelohde determinations, dilutions were made in the viscometer and the solutions agitated intermittently for short periods (10–15 min.), whereas for the Ostwald measurements all solutions were shaken for 18 hr. before use. Prolonged agitation may be necessary to establish the aggregation equilibrium between single and double molecules for a given concentration. It was noted that the differences between reduced viscosities

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for the two viscometers at similar concentrations and shear rates increased with decreasing concentration.

In conclusion, it may be said that no detectable increase in the slope constant of the Huggins equation was found for a series of polymers with known amounts of branching when measurements were made at a constant shear rate. Although this observation is contrary to theoretical predictions (14), it is recognized that the concentrations employed are such that polymer–polymer interactions will be of importance. Statistical treatments of the hydrodynamic behavior of long chain molecules are usually applied to the idealized condition that the particles are well separated in the solvent. The important difference in behavior between branched and linear molecules appears to be their relative dependence of viscosity on the shear gradient.

ACKNOWLEDGMENTS

The author is indebted to Mr. S. Wasniewski and Mr. K. Parker for technical assistance.

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THE VIBRATIONAL SPECTRA OF ISOBUTANE AND ISOBUTANE-d_1 [1]

By J. C. Evans[2] and H. J. Bernstein

ABSTRACT

The Raman spectra of liquid $(CH_3)_3CH$ and $(CH_3)_3CD$ were obtained photoelectrically and intensities and depolarization ratios measured. The infrared spectra of the corresponding gases were obtained from 3 to 35 μ. A vibrational assignment consistent with depolarization ratios and band contours has been made for the molecules on the basis of C_{3v} symmetry and their spectra correlated.

INTRODUCTION

The vibrational spectrum of isobutane has been the subject of many investigations (7) and several ambiguities remain with regard to vibrational assignments (7). Sheppard and Simpson (7) suggest that further experimental work is required to decide upon the frequency assignment of the deformation modes and the asymmetrical skeletal stretching mode. In order to clarify the situation with regard to this molecule the Raman spectra of liquid $HC(CH_3)_3$ and $DC(CH_3)_3$ have been obtained with depolarization ratios, and the infrared spectra of the vapors have also been examined. The infrared spectrum of the heavy isobutane has been reported previously (2) but no attempt at assignment was made.

EXPERIMENTAL

Isobutane was obtained from a commercial cylinder and the deuterium-substituted compound prepared by Dr. L. C. Leitch.

The Raman spectra of the liquids were obtained at $-70°$C. in a tube previously described (3) and depolarization ratios measured by comparing spectra obtained first with polaroid film wrapped with its axis parallel to the sample tube and then perpendicular to it. These ratios were corrected for the non-rectilinear irradiation set-up by the method of Rank and Kagarise (6). The mercury 4358 line was used to excite the Raman spectra, the Stokes lines of which are shown in Fig. 1. The photoelectric Raman spectrometer used (8) was operated under the following conditions: slits $\sim$10 cm.$^{-1}$, dynode voltage $=500$ v., with intermediate values of gain and response time. The current in the water-cooled mercury arcs was 17 amp.

The infrared spectra were obtained with a Perkin Elmer Model 112 double pass infrared spectrometer with LiF, NaCl, and CsBr optics. The spectra shown in Figs. 2 and 3 were obtained in a 10 cm. cell at the various pressures and slit widths indicated.

DISCUSSION

Before attempting an assignment for this molecule it is worth while mustering all the information provided by theory. Symmetry considerations limit the discussion of the point group symmetry to either C_3 or C_{3v}. Since steric hind-

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[2]*Postdoctorate Research Fellow 1953-55.*

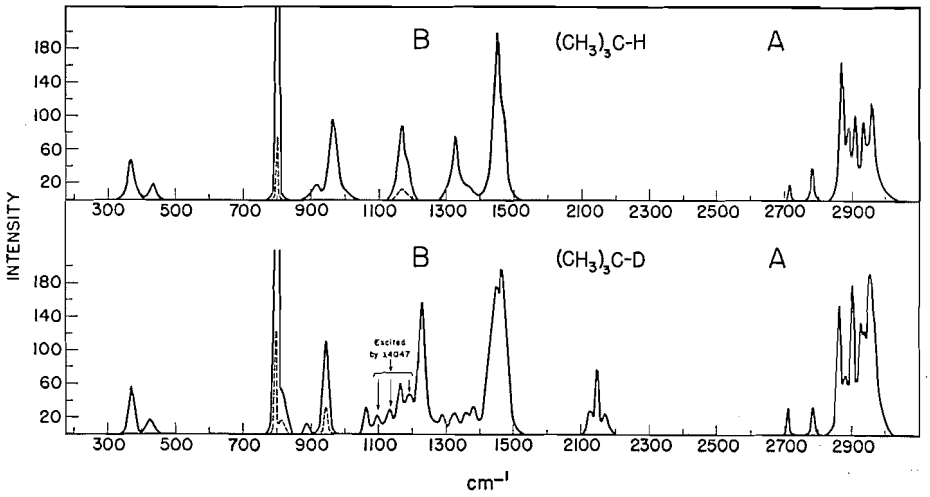

FIG. 1. Raman spectra of light and heavy isobutane.
A: slits 5 cm.$^{-1}$;
B: slits 6 cm.$^{-1}$,
—intensity scale 6× that for field A,
----intensity scale the same as for field A.

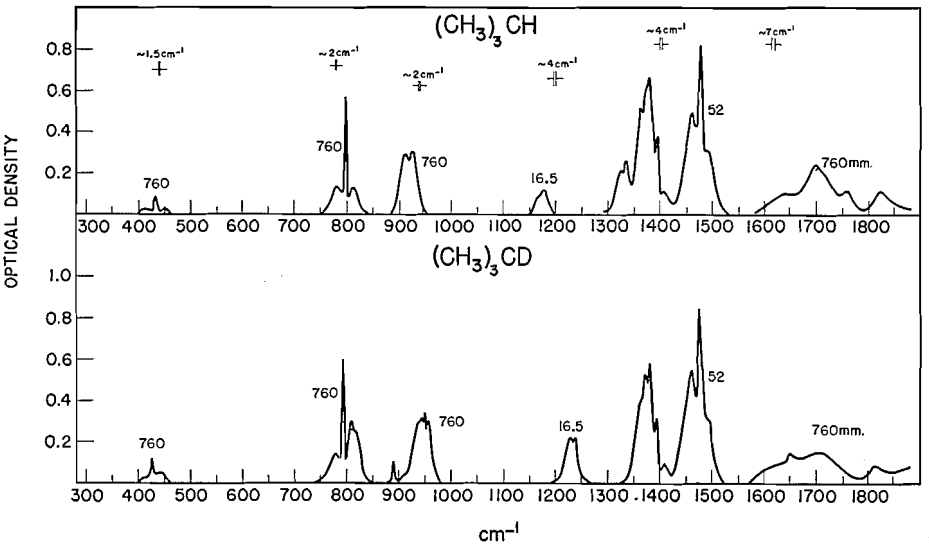

FIG. 2. Infrared spectra of gaseous light and heavy isobutane in the region 300–1800 cm.$^{-1}$.

rance probably rotates the CH_3 groups so that the planes of symmetry of the C_{3v} group are no longer present, one should actually consider isobutane to have the point group symmetry C_3 with the division of fundamentals into $12A+12E$ with all modes active in both Raman effect and infrared absorption. For all practical purposes however we shall consider the molecule to have the higher symmetry of C_{3v} to describe its vibrational spectrum, in accord with

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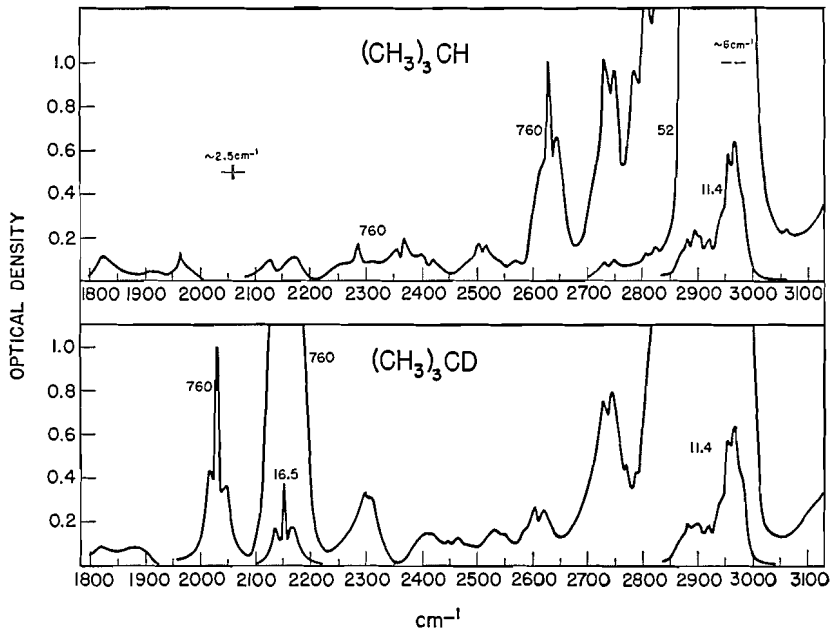

FIG. 3. Infrared spectra of gaseous light and heavy isobutane in the region 1800–3100 cm.$^{-1}$.

previous investigators (7), for which the fundamentals fall into the grouping $8A_1+4A_2+12E$. In this case the $4A_2$ type fundamentals are forbidden in both Raman effect and infrared absorption.

In order to understand the nature of the vibrational spectrum a little more clearly it simplifies matters to consider first the molecule in which the three H atoms of each CH_3 group are replaced by a single particle X. For this molecule then all bending vibrations involving X are external bending modes of the CH_3 group; the only internal mode for the CH_3 group in this molecule corresponds to the stretching vibration ν_{CX}. For the molecule $HC(CX)_3$ of point group C_{3v} there are $5A_1+1A_2+6E$ modes. It is readily seen that the distribution of the bending modes of the X group and, correspondingly, the CH_3 group is $1A_1+1A_2+2E$. In Table I the modes of vibration of isobutane have been classified according to the approximate description of internal and external modes of the CH_3 group and also in terms of other groups in the molecules. Since the internal modes of the CH_3 group are well known (7) and give rise to bands at ~3000 cm.$^{-1}$, 1450 cm.$^{-1}$, and 1350 cm.$^{-1}$, the observed spectrum will be simplified to the extent that the 10 active internal modes of the CH_3 group will appear in the spectrum at the three regions indicated. The remaining bands of the spectrum should belong to the three external bending modes of the CH_3 group and the six modes of the H—C(—C)(—C) group; the E type torsional mode being rarely observed and the A_2 type not allowed. From considerations of this kind we readily see that the isobutane molecule

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TABLE I

Species	No.		CH_3 external	CH_3 internal
A_1	ν_1			ν_{CH} unsym.
	ν_2			ν_{CH} sym.
	ν_3	ν_{CH}		
	ν_4			δ_{CH_3} unsym.
	ν_5			δ_{CH_3} sym.
	ν_6		δ_{CCH_3}	
	ν_7	ν_{CC}		
	ν_8	δ_{CCC}		
E	ν_9			ν_{CH} unsym.
	ν_{10}			ν_{CH} unsym.
	ν_{11}			ν_{CH} sym.
	ν_{12}			δ_{CH_3} unsym.
	ν_{13}			δ_{CH_3} unsym.
	ν_{14}			δ_{CH_3} sym.
	ν_{15}	δ_{CH}		
	ν_{16}		δ_{CCH_3}	
	ν_{17}		δ_{CCH_3}	
	ν_{18}	ν_{CC}		
	ν_{19}	δ_{CCC}		
	ν_{20}		Torsion	
A_2	ν_{21}			ν_{CH} unsym.
	ν_{22}		δ_{CCH_3}	
	ν_{23}			δ_{CH_3} unsym.
	ν_{24}		Torsion	

which has 36 degrees of vibrational freedom would be expected to give an observed spectrum of only 12 bands. Further in the Raman spectrum the A_1 type will be polarized and the E type depolarized and in the infrared spectrum of the gas the A_1 type will be parallel with a PR separation* of about 32 cm.$^{-1}$ and a pronounced Q branch (1), whereas the E type bands are perpendicular with less pronounced Q branch (1) and varying spacing due to Coriolis interaction (4).

Finally the Teller–Redlich product rule for isotopic substitution (4) may be used as a final check on the assignment since the theoretical product rule ratios† for the A_1 species is 1.403 and for the E type, 1.382.

The observed Raman spectra and infrared spectra are tabulated and the bands assigned for isobutane and heavy isobutane in Tables II and III respectively, and in Table IV the spectra have been correlated.

It is apparent that the depolarization ratios and infrared band contours unambiguously determine the species of the skeletal deformation modes. The question as to which frequency is to be associated with the degenerate skeletal stretching mode cannot be answered unambiguously since strong coupling in the deuterated molecule makes it impossible to use the isotopic shift as criterion.

**The PR doublet separation was calculated from the formula of Gerhard and Dennison, Phys. Rev. 43: 197. 1933. The moments of inertia of isobutane were calculated assuming $\nu_{CH} = 1.09$, $\nu_{CC} = 1.54$, with all angles tetrahedral and gave*

$$I_A = I_B = 107\times10^{-40} \text{ c.g.s. units},$$
$$I_C = 183\times10^{-40} \text{ c.g.s. units}.$$

For deuterium-substituted isobutane

$$I_A = I_B \doteqdot 110\times10^{-40} \text{ c.g.s. units}.$$

†The moments of inertia required here were those given in footnote (*).

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TABLE II

RAMAN SPECTRA OF LIQUID $HC(CH_3)_3$ AND $DC(CH_3)_3$

$\Delta\nu_a$	Isobutane			Assignment	Heavy isobutane		
	$\Delta\nu$	Int.[b]	ρ[c]		$\Delta\nu$	Int.[b]	ρ[c]
2960 (12D)	2958	116	D	ν_9, ν_{10}, ν_{11} (e)	2956	116	D
2936 (5p)	2933	94	0.27	ν_1, (a_1)	*2938	74	0.57
					2927	80	0.43
2908 (6p)	2907	103	0.18	ν_2 (a_1)	2903	108	0.25
2891 (2)	2889	87	0.38	$2\nu_{12}$ or $2\nu_{13}$ (A_1)	2882	42	0.25
2869 (12p)	2869	167	0.13	ν_3 (a_1)	2146	50	0.41
				($\nu_4+\nu_5$ A_1)	2864†	87	0.23
2778 (2p)	2783	38	0.58	$2\nu_{12}$ or $\nu_{12}+\nu_{13}$ (A_1)	2782	20	0.57
2714 (5p)	2716	19	0.10	$2\nu_{14}$ (A_1)	2712	19	0.13
	~1468	16	?	ν_4 (a_1)	1463	30	0.8
1452 (7b)D	1450	35	D	ν_{12}, ν_{13} (e)	1450	28	D
				ν_5 (a_1)	1380	6	D
1322 to (3b)D	~1373	3	?	ν_{14} (e)	1358	2	?
1355	1327	13	D	ν_{15} (e)	944	18	D
	1184	8	?	ν_6 (a_1)	1166	10	P
1172 (4b)D	1169	15	D	ν_{16} (e)	1229	25	D
965 (4b)D	966	16	D	ν_{17} (e)	1065	6	D
	917	3	D	ν_{18} (e)	813	~5	D?
795 (10)P	799	76	0.24	ν_7 (a_1)	796	70	0.17
437 (2)P	433	3	0.35	ν_8 (a_1)	426	3	0.23
371 (4b)D	367	8	D	ν_{19} (e)	370	9	D
1098 ($\frac{1}{2}$b?)	Not observed			ν_3 excited by λ4047			
					1326‡	4	
				?	1289	4	
				?	891	2	
				ν_1 excited by λ4047	1196	1	
				ν_2 excited by λ4047	1137	1	
				ν_3 excited by λ4047	1096	1	
				?	2168	~10	0.53
				?	2127	~12	0.49

[a] *Raman spectrum given in Kohlrausch, "Ramanspektren", Edwards Bros., Ann Arbor, Mich., 1945, p. 209.*

[b] *Peak heights are given on the same scale for both molecules.*

[c] *These depolarization ratios have been corrected for convergence error. P = polarized, D = depolarized = 0.87.*

* *Fermi resonance with* $2\nu_4$ (A_1).

† $\nu_4+\nu_5$ (A_1) *is a possible explanation for the intensity of 87 at 2864 cm.*$^{-1}$ *in the spectrum of* $DC(CH_3)_3$*: also incomplete deuteration. However since the largest change in intensity on deuterium substitution occurs here, i.e. from 167 in the light compound to 87 in the heavy, this band must be identified with the CH stretching mode where deuterium substitution is involved.*

‡ *Due to incomplete deuteration, i.e.* $CH(CH_3)_3$ *impurity.*

3000–1500 cm.$^{-1}$ *Region*

From the intensities in Table II it is readily seen that the band at 2869 cm.$^{-1}$ in the light compound has become very much weaker in the deuterated compound compared to the intensities of the other bands in this region. This enables one to identify this frequency with the stretching of the tertiary CH bond. In the infrared spectra the situation is not so simple and indeed it would be very difficult to make this assignment on the basis of infrared data alone. The assignments of the gas frequencies in the infrared are complicated by the extensive overlapping and therefore cannot be considered final. In Table III however this attempt has been made in accordance with expected contours. All observed bands in this region have been assigned except the very

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TABLE III

INFRARED SPECTRA OF GASEOUS ISOBUTANE AND ISOBUTANE-d_1

$HC(CH_3)_3$				Assignment	$DC(CH_3)_3$			
ν, cm.$^{-1}$	Int.	Type	*PR* separation		ν, cm.$^{-1}$	Int.	Type	*PR* separation
2980					2980			
—	w.	(∥)	~40	$2\nu_4$ (A_1)	—	w.	(∥)	~40
~2940 sh					~2940			
2968					2968			
2956	s.	(⊥)		ν_9, ν_{10}, ν_{11} (e)	2956	s.	(⊥)	
—					—			
2920	s.	(∥)		ν_1 (a_1)	2920	s.	(∥)	
2904					2904			
~2920					~2920			
2904	s.	(∥)	~26	ν_2 (a_1)	2904	s.	(∥)	~26
2894					2894			
—					2166			
2880	m.	(∥)		ν_3 (a_1)	2152	s.	(∥)	32
2872 sh					2134			
~2824 sh					—			
2806	w.	(∥)		$2\nu_{12}$ or $\nu_{12}+\nu_{13}$ (A_1)	2788	w.	(∥)	
2785					2768			
2748					2744			
2730	w.	(⊥)		$\nu_5+\nu_{13}$ (E)	2730	w.	(⊥)	
2645					—			
2629	w.	(∥)		$\nu_4+\nu_6$ (A_1)	2620	w.	(∥)	
~2616					2604			
2570	v.w.			?	2584	v.w.		
				?	2550	v.w.		
				?	2535	v.w.		
2516	w.			$\nu_6+\nu_{14}$ (E)				
2502								
2480 sh	w.			?	2464	v.w.		
				?	2446	v.w.		
2422	v.w.	(⊥)		ν_5+unperturbed ν_{17} (E)?	2410	v.w.		
2402								
2371								
2357	w.	(∥)		$2\nu_6$ (A_1)				
—								
~2310					~2310			
2286	v.w.	(∥)		$\nu_4+\nu_7$ (A_1)	~2298	v.w.	(∥)	
~2265								
2170	v.w.			$\nu_5+\nu_7$ (A_1)				
2125				$\nu_7+\nu_{14}$ (E)				
					2046			
				2×unperturbed ν_{17} (A_1)?	2030	m.	(∥)	28
					2018			
1967	v.w.			$\nu_6+\nu_7$ (A_1)				
				$\nu_8+\nu_{12}$, $\nu_8+\nu_{13}$ (E)	1885	v.w.		
1910	v.w.			$\nu_4+\nu_8$ (A_1)				
1821	v.w.			$\nu_5+\nu_8$ (E)	~1814	v.w.		
1760	v.w.			$\nu_5+\nu_{19}$ (E)				
1720	v.w.			$\nu_{14}+\nu_{19}$ (A_1)	1710	v.w.		
1698	v.w.			ν_8+unperturbed ν_{15} (E)				
1644	v.w.			ν_{19}+unperturbed ν_{15} (A_1)?	1650	v.w.		
				?	1620			
1493					~1492			
1477	s.	(∥)	32	ν_4 (a_1)	1477	s.	(∥)	31
1461					1461			
1406					1410			
1394	m.	(∥)	~35	ν_5 (a_1)	1394	s.	(∥)	~37
~1371					~1373			
1379	s.	(⊥)		ν_{14} (e)	1379	m.	(⊥)	
1362					1362			
1334	m.	(⊥)		ν_{15} (e)	956	s.	(⊥)	
1325					947			

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TABLE III (*concluded*)

INFRARED SPECTRA OF GASEOUS ISOBUTANE AND ISOBUTANE-d_1

$HC(CH_3)_3$				Assignment	$DC(CH_3)_3$			
ν, cm.$^{-1}$	Int.	Type	*PR* separation		ν, cm.$^{-1}$	Int.	Type	*PR* separation
1177	m.			ν_6 (a_1)				
~1166	m.			ν_{16} (e)	1238, 1228	s.	(⊥)	
				$\nu_{14} - \nu_3$ (E)	942, 935 sh	m.	(⊥)	
925, 912	s.	(⊥)		ν_{18} (e)	817, 808	m.	(⊥)	
				?	~ 907, 890	w.	?	
811, 797, 781	s.	(∥)	30	ν_7 (a_1)	— ~ 810, 793, 779	s.	(∥)	31
~ 445, 426, ~ 412	m.	(∥)	~33	ν_8 (a_1)	448, 432, ~ 413	m.	(∥)	~35

TABLE IV

VIBRATIONAL ASSIGNMENTS

		$HC(CH_3)_3$		$DC(CH_3)_3$		Product rule ratios	
		Raman liquid	Infrared gas	Raman liquid	Infrared gas	Theor.	Obs. (Raman)
A_1	ν_1	2933	2920	2927	2920	1.40	1.39
	ν_2	2907	2904	2903	2904		
	ν_3	2869	2880	2146	2152		
	ν_4	1468	1477	1463	1477		
	ν_5	1373	1394	1380	1390		
	ν_6	1184	1177	1166			
	ν_7	799	797	796	793		
	ν_8	433	426	426	432		
E	ν_9	2958	2962	2956	2962	1.38	1.37_5
	ν_{10}	2958	2962	2956	2962		
	ν_{11}	2958	2962	2956	2962		
	ν_{12}	1450	~1475	1450	~1475		
	ν_{13}	1450	~1475	1450	~1475		
	ν_{14}	~1373	1371	1350	1367		
	ν_{15}	1327	1330	944	952		
	ν_{16}	1169[a]	1166	1229	1233		
	ν_{17}	966[a]		1065	—		
	ν_{18}	917[a]	918	813	812		
	ν_{19}	367	—	370	—		

[a] *Assignment of K. S. Pitzer and J. E. Kilpatrick, Chem. Revs. 39: 435. 1946.*

weak features at 1620, 2446, 2464, 2535, 2550, and 2584 cm.$^{-1}$ in the infrared spectrum of $DC(CH_3)_3$, and the very weak band at 2570 in the infrared spectrum of $HC(CH_3)_3$. In the Raman spectrum of $DC(CH_3)_3$ the bands at 2127 and 2168 cm.$^{-1}$ are difficult to assign on the basis of the observed fundamentals.

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Region Below 1500 cm.$^{-1}$

In this region there is little difficulty in assigning the bands between 1480 and 1300 cm.$^{-1}$ but comparison of the spectra of the light and heavy molecules between 1300 and 800 cm.$^{-1}$ shows very little resemblance to what one would expect for this particular deuterium substitution. In Fig. 1 for example the strong band at 1169 in the light compound seems to have been shifted to higher wave number on deuterium substitution whereas the band at 966 cm.$^{-1}$ although shifted in the expected direction to lower wave number has moved too much if the shift in ν_7 is a criterion. In Fig. 2 the anomalous isotopic shifts are even more pronounced in the bands at ~1180 cm.$^{-1}$ and 918 cm.$^{-1}$. There can be no question that there is strong interaction or coupling between these vibrational modes.

One possible set of interactions to account for the observed spectrum is the following. If the bands at 1169 and 1320 cm.$^{-1}$ in the light compound are coupled, the unperturbed position of 1169 may be in the region to give the band at 1229 cm.$^{-1}$ in the deuterated compound. The unperturbed position of the CH deformation mode at 1327 cm.$^{-1}$ would fall perhaps to ~900 cm.$^{-1}$ upon deuterium substitution. This band would be strongly coupled with the unperturbed band at 917 cm.$^{-1}$ (which should be relatively undisplaced in the deuterium compound), to give rise to the bands at 813 and 944 cm.$^{-1}$. Since all bands are strongly coupled in the light compound the unperturbed position of 966 cm.$^{-1}$ may give rise to the band observed at 1065 cm.$^{-1}$ in the heavy compound. The band observed at 1166 cm.$^{-1}$ in the heavy compound is the polarized band arising from the polarized band at 1184 cm.$^{-1}$ in the light compound; this band does not participate in the coupling because it is of different symmetry species from the others. If this coupling system is sensible the ratios to be taken in calculating the product rule are

$$\frac{917}{813} \times \frac{966}{1065} \times \frac{1169}{1229} \times \frac{1327}{944}.$$

Rigorously the product of the ratios of the frequencies of the unperturbed band should be taken but since the interaction displaces bands in pairs by equal amounts in opposite directions and since these displacements are small compared to the band positions the ratios of the observed frequencies might be expected to be very nearly the same as those for the unperturbed values.

Since the change in frequency of all modes other than ν_{15} is expected to be negligible on deuterium substitution the observed product rule ratio will be given by the product of the ratios of the frequencies of the coupled bands. This ratio is calculated to be 1.37_0 which is consistent with the theoretical value of 1.38 given above for the E type modes. It is apparent that assignment of one of 917, 966, and 1169 cm.$^{-1}$ to the degenerate skeletal mode is not forthcoming from the present data; however if the suggested coupling scheme is indicative of the true state of affairs the mode at 1169 cm.$^{-1}$ which has an unperturbed frequency in the twelve hundreds is not a likely candidate for this assignment.

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The observed infrared spectrum in the region below 1500 cm.$^{-1}$ has been assigned except for the weak band at 890 cm.$^{-1}$ in $CD(CH_3)_3$ whereas in the Raman spectrum of $DC(CH_3)_3$ the corresponding band at 891 cm.$^{-1}$ and the bands at 1289 cm.$^{-1}$ remain unexplained. The assignment is essentially the same as that of Pitzer and Kilpatrick (5) differing in the following respects:

(i) The A_1 wag of the CH_3 group ν_6 is given here as the Raman band at 1184 cm.$^{-1}$ in preference to the band at 1098 cm.$^{-1}$ which we did not observe in the Raman spectrum. The latter band is probably ν_3 excited by λ4047.

(ii) We have assigned the CH stretching mode frequencies which were all taken as 2950 cm.$^{-1}$ by Pitzer and Kilpatrick for the purpose of thermodynamic calculations.

The present assignment will not alter materially the results of the thermodynamic calculations (5) since the uncertainty introduced in assigning the A_2 wag (ν_{22}) is certainly as large as the present change in vibrational frequencies.

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ADSORPTION OF OXYGEN BY A SILVER CATALYST[1]

By W. W. Smeltzer,[2] E. L. Tollefson,[3] and A. Cambron[4]

ABSTRACT

An apparatus is described to measure volumetrically the amount of gas adsorbed by a catalyst at constant pressure and at exposure times as short as 0.1 min. The volumes of oxygen adsorbed by a technical silver catalyst at pressures of 200, 400, and 700 mm. and in the temperature range of 180° to 300° C. have been measured. Surface area determinations of 0.33 to 0.38 sq. meter per gm. of catalyst by physical adsorption and chemisorption methods show that each silver atom of the surface is associated with approximately one oxygen adatom at a monolayer coverage. The initial rate of adsorption of oxygen is directly proportional to its pressure. Observed transitions in the oxygen adsorption rates indicate that more than one type of oxygen complex occurs on the catalyst surface. The Elovich equation provides the best approximation of the adsorption rate data but is of limited applicability in interpretation of the mechanism of adsorption. Values of 22–29 kcal./mole and 17–25 kcal./mole have been calculated for the apparent activation energy and isosteric heat of adsorption respectively.

INTRODUCTION

Investigations by Twigg (13, 14) and Orzechowski and MacCormack (8) on the oxidation of ethylene to ethylene oxide and carbon dioxide over a silver catalyst have emphasized the role played by the chemisorption of oxygen in the reaction kinetics. There is, however, meager information about the oxygen adsorption characteristics of silver at elevated temperatures. As part of a program designed to elucidate some of the properties of a technical silver catalyst used in the oxidation of ethylene, the rates of adsorption and volumes of chemisorbed oxygen have been determined as a function of pressure and temperature in this investigation. The results reported are for the operating temperatures and oxygen partial pressures used in reaction studies with a silver catalyst prepared by the method of Cambron and McKim (5).

Thus far, probably the most extensive investigation has been made by Benton and Drake (2) who examined the adsorption of oxygen in the temperature range of −183° C. to 200° C. by a silver catalyst prepared from precipitated silver oxide. Two types of adsorption were found, namely, a practically instantaneous physical adsorption at −183° C. which decreased rapidly with increasing temperature and an activated adsorption which proceeded slowly at 0° C. and increased rapidly at higher temperatures to give a saturation volume nearly independent of temperature over the range of 150° to 200° C. For this latter type of adsorption, the values of the isosteric heat of adsorption and energy of activation were 23–15 kcal./mole and 12.7 kcal./mole respectively.

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With the exception of this investigation, little appears in the literature on the adsorption of oxygen by silver at elevated temperatures. Taylor (11) measured the rate of oxygen uptake by silver in the temperature range of 0° to 184° C. and found that the energy of activation decreased with increasing adsorption from 17 to 13 kcal./mole. Twigg (13) found that the change in the electrical resistance ΔR of a silver plated glass wool catalyst increased in the presence of oxygen at a pressure p according to the relationship

$$\Delta R = a\sqrt{p}/(1+b\sqrt{p}), \quad [1]$$

where a and b are constants. Applying values for the solubility of oxygen in silver reported by Steacie and Johnson (10), Twigg was led to the conclusion that the resistance effect was caused primarily by oxygen adsorption. Attempts have been made to determine the number of oxygen atoms complexed with each surface silver atom. Buttner, Funk, and Udin (4) measured the surface tension of solid silver in helium–oxygen mixtures between 870° and 945° C. Using the data with the Gibbs adsorption isotherm, these authors concluded that 1.4 atoms of oxygen were associated with each silver atom at 932° C. Armbruster (1) measured the adsorption of oxygen by silver foil of preferred crystalline orientation in the temperature range of −195° to 20° C. The data were satisfactorily represented by the Langmuir isotherm. Using the calculated monolayer volume, this author concluded that one oxygen molecule was associated with four silver atoms. Since few data are available on the kinetics of oxygen chemisorption on silver above 150° C. and because the oxygen–silver atom ratio shows apparent variations with temperature, the adsorption of oxygen at exposure times as low as 0.1 min. has been measured in the temperature range of 180° to 300° C. in this investigation.

EXPERIMENTAL

Catalyst Preparation

Catalyst I was prepared from an alloy of silver containing 11.3% calcium and 0.11% nickel. A powdered sample in the mesh size range −35 +65 was activated by a steam exposure at 305° C. for seven hours to oxidize the calcium, a leach in boiling 20% acetic acid for four hours, and finally a thorough washing in distilled water. This activation procedure was repeated. Chemical analysis showed that the catalyst contained less than 0.05% calcium and 0.001% nickel. A charge of 49.0 gm. of this catalyst was placed in the adsorption cell.

Catalyst II was prepared from an alloy of silver containing 10.0% calcium, 0.14% nickel, and 0.14% copper. A powdered sample in the mesh range −20 +35 was activated by the above procedure. Chemical analysis showed that the catalyst contained 0.08% nickel, 0.13% copper, and 0.08% calcium. A charge of 50.0 gm. of this catalyst was placed in the adsorption cell.

Catalyst Reference State

In order that the catalyst surface would be in the same reference state before each adsorption run, a standard evacuation temperature of 300° C. was chosen since a reasonable rate of desorption occurred without injury to

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the catalyst by sintering. A standard pumping time of 20 hr. was adopted after it was established that the volume of oxygen adsorbed after 40 hr. pumping was the same, within experimental error, as that after 20 hr. for the same experimental conditions.

Apparatus and Procedure

The apparatus for the determination of the gas volumes adsorbed by the silver catalyst at various temperatures and oxygen pressures consisted essentially of an adsorption cell connected to a gas burette and a mercury manometer. With the exception of the pressure control device, the vacuum system was of conventional design and consisted of pressure gauges, an oxygen and argon purification train and storage, a mercury diffusion pump, and other standard accessories.

The furnace, which was positioned around the adsorption cell by a slide, consisted of a 12 in. × 4 in. diameter aluminum cylinder of 1 in. wall thickness wound with a monel heating element and insulated with magnesia. The electrical current through the heater was regulated by a Bristol temperature controller which maintained the catalyst temperature within ±1° C. The temperature of the adsorption cell was measured by two standardized chromel–alumel thermocouples fixed inside the furnace.

Fig. 1 illustrates the adsorption section of the apparatus. The adsorption cell was connected to the gas burette by a short tube and a standard 3 mm. stopcock. To allow for end effects of the furnace on the apparent volume of the adsorption cell, the dead space calibrations were made at the experimental

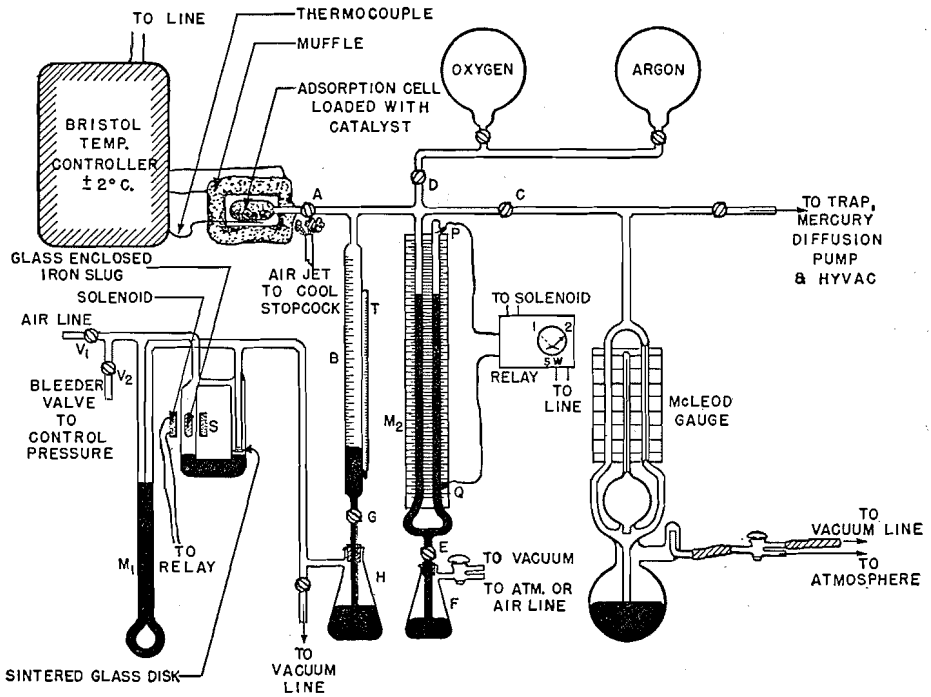

FIG. 1. Diagram of adsorption apparatus.

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temperatures with argon. The automatic pressure control device was included in this section of the apparatus to permit burette readings in rapid succession at constant pressure. For this purpose, manometer M_2 was equipped with electrical contacts P and Q and these were connected to the grid circuit of a tube driving a relay. The output of this single pole double throw relay was such that the action of the grid circuit could be reversed. If the output circuit was closed, the solenoid S was energized and raised the glass-enclosed iron slug; simultaneously the mercury level was lowered away from the sintered glass disk in the pressure control device. Thus, air flowed through the disk and raised the mercury in the gas burette when a pressure existed below the control pressure.

Prior to the performance of an adsorption experiment, the standard desorption procedure was performed. The furnace temperature was then set to the desired value and stopcocks A, C, and D were closed. The mercury in burette B was lowered and the manometer M_2 was adjusted so that the column of mercury would contact point P when the system was brought to the run pressure. Stopcock E was then closed and oxygen was admitted through stopcock D from the storage bulb until the mercury in manometer M_2 registered slightly less than the desired run pressure. At this stage, pressure was applied to the mercury surface in flask H by using the relay arrangement. When the stopcock G was opened, the mercury in the gas burette rose until it was automatically stopped when electrical contact was made between the lead P and the mercury column in manometer M_2. After values of the temperature, pressure, and volume had been recorded, the mercury in the burette was raised by a volume equal to that of the dead space of the adsorption cell. An appropriate air pressure differential was then established across manometer M_1 and stopcock A was opened. The volumes of adsorbed oxygen at constant pressure were recorded by burette readings at 0.1 min. intervals or longer.

Materials

The silver–calcium alloys were prepared from high purity Royal Mint silver and high purity calcium supplied by Dominion Magnesium Limited. The minor alloying constituents were prepared from high purity electrolytic copper and Merck nickel shot of 98–99% purity.

The argon and oxygen gases were obtained from commercial cylinders of the Dominion Oxygen Company with a specified purity of at least 99.7%. Prior to storage in the adsorption apparatus these gases were passed through a purification train consisting of ascarite to remove carbon dioxide, heated platinized asbestos in the case of oxygen to remove hydrogen, heated copper in the case of argon to remove oxygen, phosphorus pentoxide to remove water vapor, and a trap at liquid air temperature to remove residual condensible vapors.

RESULTS

The catalyst surface should maintain the same area and properties during the course of experimentation in order that an analysis can be made of the oxygen adsorption results at different temperatures and pressures. Fig. 2 shows the volumes of oxygen adsorbed by Catalyst I with a given set of experimental

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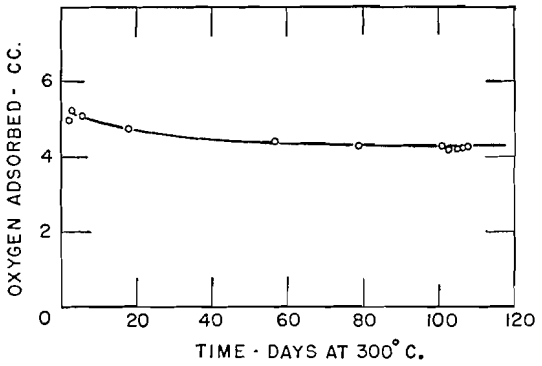

FIG. 2. Adsorption of oxygen by Catalyst I at 260° C. and 400 mm. pressure after evacuation of the catalyst at 300° C. for different time periods.

conditions after the standard evacuation. The volume adsorbed at 400 mm. pressure and 260° C. after the catalyst was maintained at 300° C. for 100 days is approximately 81% of the initially adsorbed volume. Furthermore, the decrease in the adsorption capacity of the catalyst during the last 55 days is less than 5% of the volume adsorbed. The extensive results presented herein for Catalyst I were taken during this period.

Illustrative plots of the volumes of oxygen adsorbed by Catalyst I versus time for each set of adsorption conditions studied in the temperature range of 180° to 300° C. are given in Figs. 3 and 4. There is an initial rapid rate of

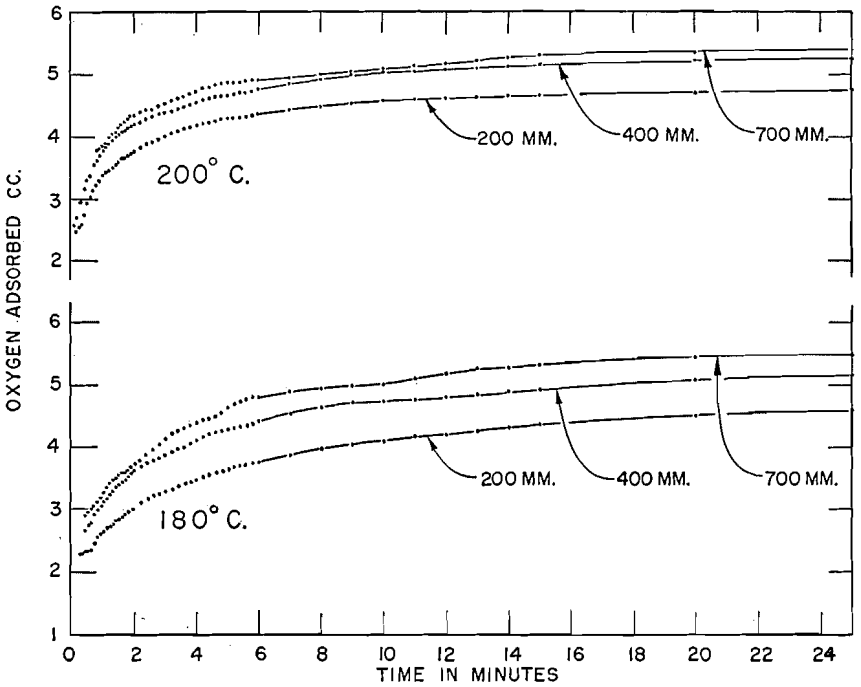

FIG. 3. Oxygen adsorption – time curves for Catalyst I at pressures of 200, 400, and 700 mm. and temperatures of 180° and 200° C.

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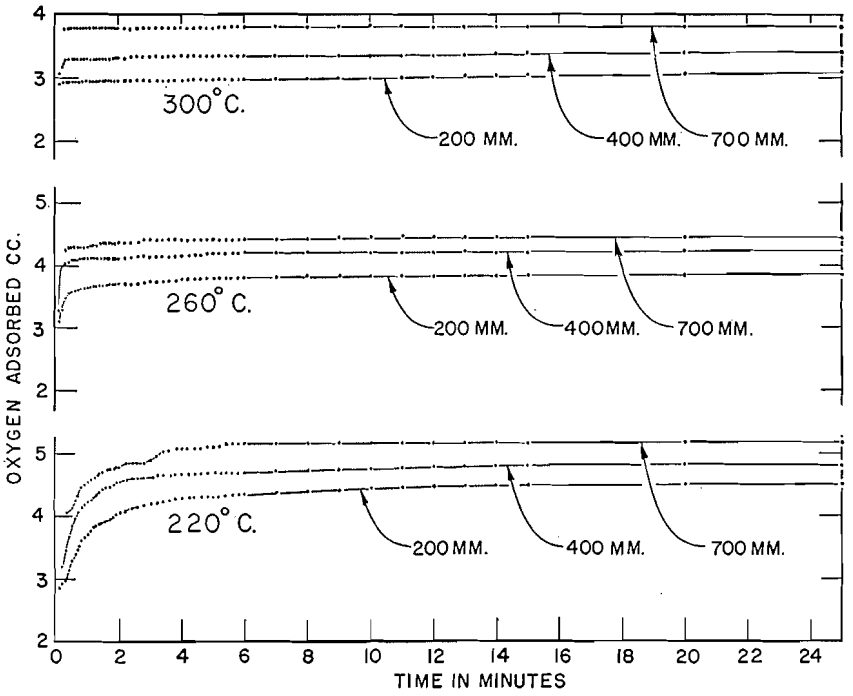

FIG. 4. Oxygen adsorption – time curves for Catalyst I at pressures of 200, 400, and 700 mm. and temperatures of 220°, 260°, and 300° C.

adsorption which increases with increasing temperature. This rate then decreases to a low value and in the temperature range of 200° to 300° C. the volumes of adsorbed oxygen approach their equilibrium values after exposures of 25 min. For example, the adsorption in this temperature range after 15 min. was at least 98% of the total volume adsorbed after 25 min. The small increase in oxygen uptake during the last 10 min. may be due partially to the solubility of oxygen in silver. Isobars of the volumes adsorbed by the catalyst after 25 min. exposure in oxygen and, also, these volumes corrected for the equilibrium solubility of oxygen in silver according to the values given by Steacie and Johnson (10) are illustrated in Fig. 5. Values are not given for 180° C. because adsorption was not complete in the experimental time.

Results for the initial rapid adsorption of oxygen by Catalyst II after exposures of 0.1 min. are illustrated in Fig. 6. Although the rate of adsorption at temperatures above 220° C. was too fast to be measured accurately because of the initial pressure drop in the system, the curves indicate that this initial rate is proportional to the oxygen pressure. Reliance cannot be placed on a comparison of the slopes of the curves at different temperatures, as the adsorption experiments were completed after the catalyst had been evacuated for only one week at 300° C. In a similar manner, the volumes of oxygen adsorbed by Catalyst I after 0.3 min. of exposure are, within the experimental precision, proportional to the oxygen pressure.

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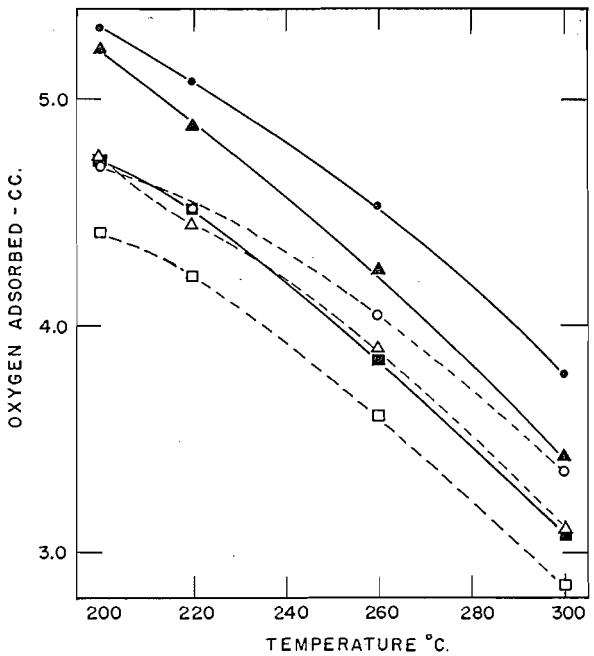

FIG. 5. Isobars of oxygen adsorption by Catalyst I.
■ ▲ ● volumes adsorbed after 25 min. at 200, 400, and 700 mm. pressure respectively with no solubility correction.
□ △ ○ volumes adsorbed after 25 min. at 200, 400, and 700 mm. pressure respectively with solubility correction.

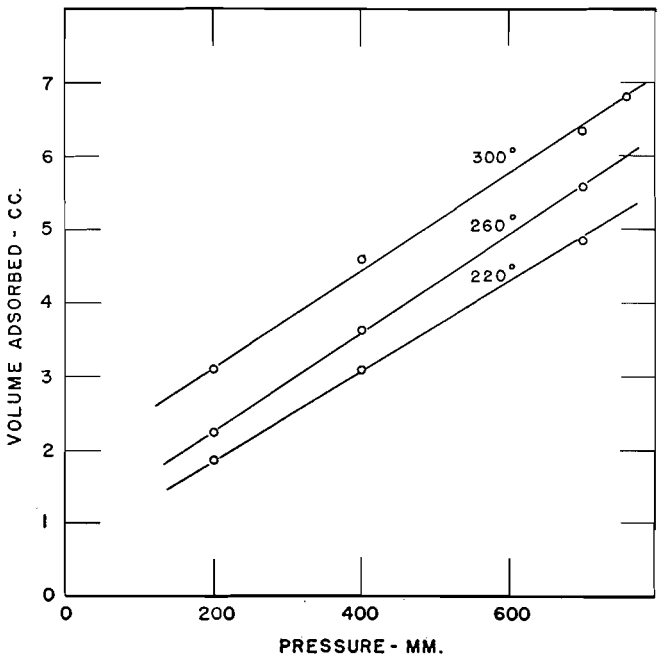

FIG. 6. Volumes of oxygen adsorbed by Catalyst II after 0.1 min. and temperatures of 220°, 260°, and 300° C.

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DISCUSSION

Surface Area and Silver–Oxygen Atom Ratio

The isobars of Fig. 5 show that the volume of oxygen finally adsorbed is larger at lower temperatures at constant pressure. This indicates a process involving a state of equilibrium between the adsorbate and the gas phase. In an attempt to determine the catalyst surface area and some properties of the adsorbate, these results are analyzed according to the Langmuir adsorption isotherm. To substantiate this approach, results privately communicated by Drs. A. Orzechowski and K. E. MacCormack on oxygen and krypton adsorption by a catalyst prepared in the same manner as used in this investigation are analyzed according to the Langmuir (7) and Brunauer, Emmett, and Teller (B.E.T.) (3) gas adsorption methods of obtaining surface areas respectively.

One form of the Langmuir isotherm equation is

$$[2] \qquad \frac{1}{V} = \frac{1}{V_m b p} + \frac{1}{V_m},$$

where p is the pressure, V the volume of gas adsorbed, V_m the volume required to complete a monolayer, and b is a constant. Plots of $1/V$ vs. $1/p$ for the values recorded in Fig. 5 are given in Fig. 7. Linear curves satisfy the results for the temperatures of 200°, 220°, and 260° C. and the pressure range studied. This is valid for both the total uptakes of oxygen and these volumes corrected for solubility of oxygen in the catalyst. The monolayer volume calculated from the intercepts in the temperature range 200°–260° C. varies from 4.8 to

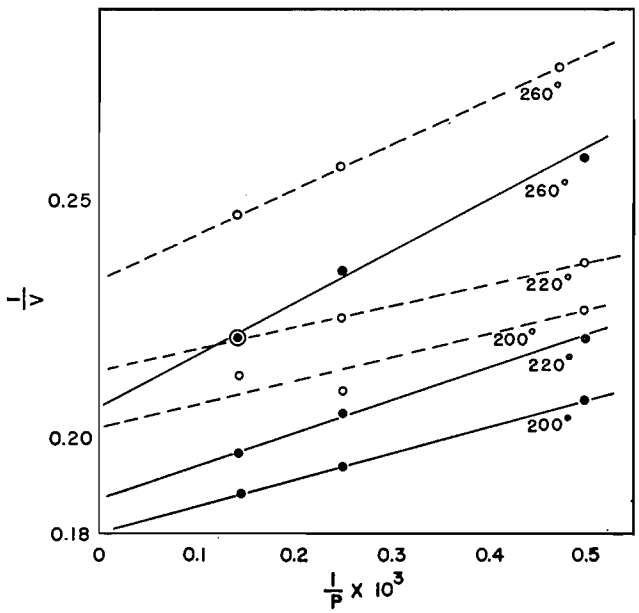

FIG. 7. Langmuir isotherm plots of adsorption data for Catalyst I.
● volumes of oxygen adsorbed after 25 min. with no solubility corrections.
○ volumes of oxygen adsorbed after 25 min. with solubility corrections.

5.6 cc. and, if oxygen solubility is taken into account, from 4.3 to 4.9 cc. Thus, V_m values deviate approximately 15% over the temperature range investigated. If the determination at 220° C. is taken as a mean value, V_m is 5.3 cc. or 4.7 cc. depending upon whether an oxygen solubility correction is made. These values (0.11 or 0.10 cc. per gm. of catalyst) correspond to areas of 0.41 or 0.37 sq. meter per gm. if it is assumed that the cross-sectional area of an oxygen molecule is 14.1 sq. Å.

Orzechowski and MacCormack determined the adsorption isotherm with krypton as the adsorbate at 77.5° K. and, also, the volume of oxygen adsorbed at 220° C. by a 40 gm. sample of catalyst under the experimental conditions employed in this investigation. A surface area of 0.36 sq. meter per gm. of catalyst was obtained from these results when they were analyzed according to the B.E.T. method with the assumption that the cross-sectional area of the krypton molecule was 21.8 sq. Å (9). A Langmuir plot of these results gave a monolayer volume of 4.0 or 3.5 cc. (0.10 and 0.09 cc. per gm. of catalyst) depending upon whether or not oxygen solubility was considered. These latter values, which correspond to surface areas of 0.38 and 0.33 sq. meter per gm., are in agreement with the values determined by the B.E.T. method and, also, with the values of 0.41 and 0.37 sq. meter per gm. determined in this investigation.

This permits a simple approximation to be made as to the number of oxygen atoms complexed with each surface silver atom. If the catalyst surface consists of cubic face-centered crystal faces, the effective area of a silver atom is 8.32 sq. Å. The B.E.T. determination of 0.36 sq. meter corresponds to 4.3×10^{18} atoms of silver. This number is equivalent to either 0.04 or 0.08 cc. of oxygen depending upon whether one or two atoms of oxygen are adsorbed by two silver atoms. The monolayer volumes ranging from 0.09 to 0.10 and 0.10 to 0.11 cc. of oxygen per gm. of catalyst determined from the results of Orzechowski and MacCormack and this investigation, respectively, indicate that one oxygen atom is adsorbed by each silver atom under saturation conditions. Despite this agreement, the calculation is only a first approximation as only one type of crystalline face has been considered.

The agreement of the values for the monolayer volume determined by a Langmuir and B.E.T. analysis does not substantiate the view that simple Langmuir considerations satisfy the characteristics of oxygen chemisorption on silver. This is so because, first, the calculated monolayer volume varies with temperature, second, the energy of adsorption is not constant, and, third, another analytical expression may be used to represent the experimental results. The Langmuir plots of Fig. 7, which do not yield a common intercept, illustrate the first limitation. An examination of the isosteric heat of adsorption, Q, may be used to illustrate the second limitation. Q may be evaluated from the equation

$$[3] \qquad Q = \frac{1}{R}\left(\frac{d \ln p}{d(1/T)}\right)_{V,\,A},$$

where R is the gas constant and p is the equilibrium pressure of a specified volume V of adsorbate at a temperature T on a surface of constant area A.

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Although the accuracy is poor, the values calculated for the isosteric heat of adsorption (using the volumes of oxygen adsorbed shown in Fig. 5 without corrections for oxygen solubilities) vary from 25 to 17 kcal./mole for surface coverages of 68 to 82%. These values, which are in agreement with those reported by Benton and Drake (2), illustrate that the isosteric heat of adsorption is not constant even at large surface coverages.

The agreement of the experimental results, which may be fitted to the Langmuir isotherm equation, with the expression

$$V = a\sqrt{p}/(1+b\sqrt{p}), \quad [4]$$

where V is the volume of adsorbed gas, p is the equilibrium pressure, and a and b are constants, illustrates the third limitation. This expression is similar to equation (1) found by Twigg (13) to satisfy the variation of the electrical resistance of silver in the presence of oxygen. To distinguish the applicability of these isotherm equations, measurements must be extended over a larger pressure range. We stress that the Langmuir isotherm equation has been applied arbitrarily over a limited pressure and temperature range to calculate the monolayer volume.

Adsorption Kinetics

In recent papers, Taylor and Thon (12) and Landsberg (6) have shown that the rates of chemisorption of several gases on solid surfaces may be represented by the Elovich equation,

$$dq/dt = ae^{-\alpha q}, \quad [5]$$

where q is the amount of gas adsorbed, t is the time, and a and α are constants. The integrated form of this equation is

$$q = (2.3/\alpha)\log(t+t_0) - (2.3/\alpha)\log t_0 \quad [6]$$

if $t_0 = 1/\alpha a$. Thus, with a correctly chosen t_0, the plot of q as a function of $\log(t+t_0)$ should give a linear curve with slope $2.3/\alpha$. Also, a, which represents the initial rate of adsorption for $q = 0$, may be evaluated. If t_0 is too small to be assigned a value, a may be evaluated from

$$q_t = (1/\alpha)\ln(1+\alpha a t) \quad [7]$$

if q_t represents the amount of gas adsorbed after time t. Orzechowski and MacCormack (8) have fitted the data of Benton and Drake (2) for the chemisorption of oxygen by silver to an equation of this type, one valid for the approximate range $0.3 < \theta < 0.5$ and another for the range $0.5 < \theta < 0.7$ where θ is the fraction of the monolayer. In each range, a was directly proportional to the oxygen pressure.

Although the adsorption versus time curves of Figs. 3 and 4 show that the Elovich logarithmic rate equation may not be expected to completely fit the adsorption results, it is advantageous to apply this equation in a discussion of the adsorption kinetics. Plots of the adsorbed volumes on Catalyst I versus the logarithm of time for the temperature range of 180° to 260° C. and an oxygen pressure of 200 mm. are shown in Fig. 8. There are, at the temperatures

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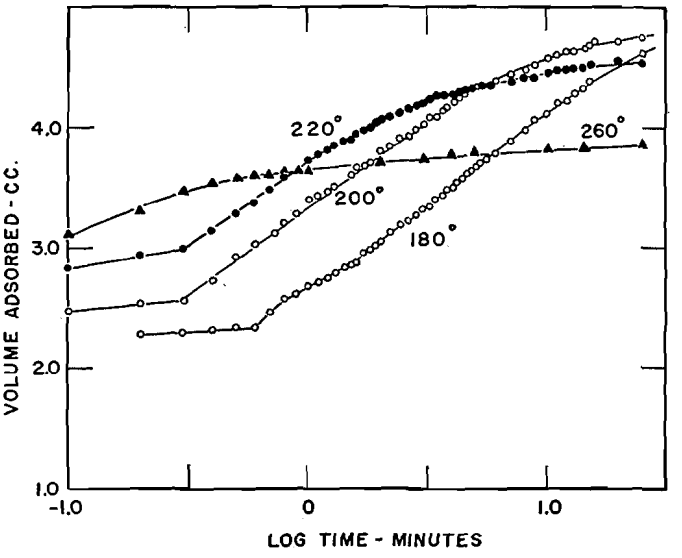

FIG. 8. Adsorption data at 200 mm. pressure for Catalyst I plotted according to the Elovich equation.

of 180°, 200°, and 220° C., abrupt changes in the slopes of the curves within the range of 2.2 to 3.0 cc. of adsorbed gas to regions of practically constant slopes. These latter slopes decrease at higher surface coverages in a manner which is more pronounced at higher temperatures. For the experimental conditions studied, the initial abrupt changes occur only at coverages corresponding to less than 3 cc. of adsorbed gas. It is assumed that α and a may be evaluated from the constant slopes and the volumes of gas adsorbed in these regions (equation [7]). These values and the surface coverages for which the curves are of approximately constant slope are recorded in Table I. Values are recorded only for the temperature range of 180° to 220° C. as the adsorption rate is too rapid at higher temperatures to determine the functional relationship with time.

The calculated values for an initial rate of adsorption, a, increase with pressure and temperature. The dependence of the rate on pressure cannot be determined because the evaluations are not sufficiently accurate. However, the results presented in Fig. 6 indicate that this rate is directly proportional to the pressure. Moreover, it is to be noted that the calculated values for this initial rate are much larger than the experimentally determined values. In Fig. 9 plots are shown of the logarithms of the calculated and experimentally determined values for the initial rate of adsorption versus the reciprocal of the absolute temperature. As a measure of the experimentally determined rate, the reciprocals of the times required to adsorb 3 cc. of oxygen on Catalyst I at 200 mm. pressure of oxygen were used. The apparent energies of activation calculated from the slopes of the least squares lines are 27–29 kcal./mole and 22 kcal./mole for the calculated and experimentally determined initial rates of adsorption respectively. This latter value of 22 kcal./mole is larger than the

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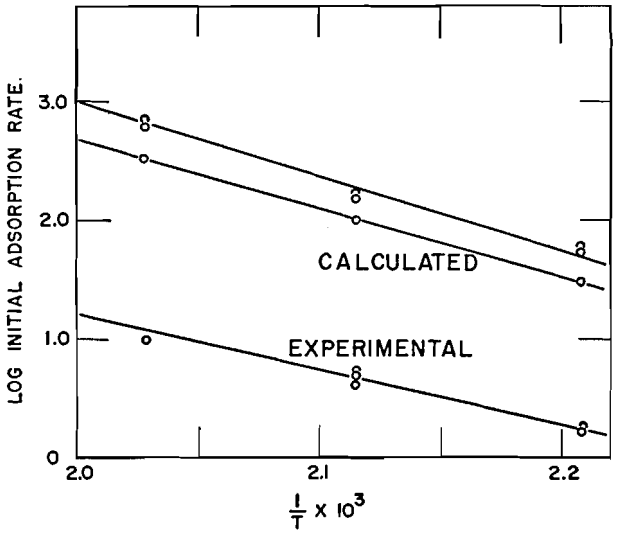

FIG. 9. Arrhenius plots of initial rates of oxygen adsorption on Catalyst I.

values of 17 to 13 kcal./mole reported by Taylor (11) and Benton and Drake (2).

The surface coverages recorded in Table I illustrate that the curves of constant slopes are confined to the approximate range $0.5 < \theta < 0.9$ if the experimental results are plotted according to the Elovich equation. In this analysis, t_0 was assumed to be equal to zero as positive values of this constant gave no better fit of the data to the equation. The above range corresponds to

TABLE I

VALUES OF CONSTANTS α AND a OF ELOVICH EQUATION AND SURFACE COVERAGE θ FOR WHICH EQUATION IS APPLICABLE

Temperature, °C.	Pressure, mm.	α, 1/cc.	a, cc./min.	θ, fraction of monolayer
180	200	1.5	30	0.5–0.8
	400	1.4	60	0.5–0.9
	700	1.3	55	0.6–0.9
200	200	1.5	100	0.5–0.8
	400	1.4	150	0.5–0.8
	700	1.4	160	* –0.9
220	200	1.7	320	0.6–0.7
	400	1.6	630	* –0.8
	700	1.5	670	* –0.9

*Not observed.

that of $0.5 < \theta < 0.7$ found by Orzechowski and MacCormack (8) from an analysis of the data on oxygen adsorption on silver at lower temperatures. Also, the abrupt changes in the slopes of the Elovich curves at a surface coverage of approximately 0.5 are similar to a break in the curve for the adsorption

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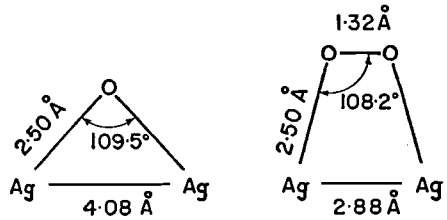
of hydrogen on zinc oxide found by Taylor and Thon (12). These authors suggest that abrupt changes in the slopes of the Elovich curves indicate a change from one kind of site to another at a certain stage of adsorption.

This investigation supports the view that more than one kind of site is involved in the chemisorption of oxygen on silver. Figs. 3 and 4 show that the curves for adsorption at 180°, 200°, and 220° C. have transitions due to differences in the adsorption rates at 0.6, 0.2, and 0.2 min. respectively after the beginning of the adsorption runs. These abrupt changes in the adsorption–time curves and the curves for data plotted according to the Elovich equation occur at approximately half coverage of the catalyst surface. This suggests that initially the surface is rapidly covered by oxygen so that each oxygen atom is associated with two silver atoms. A relatively slow rearrangement of adatoms may then occur which permits further adsorption until one oxygen atom is associated with each silver atom. If this is correct, the different kinds of adsorption sites may be associated with differences in the bonding of oxygen with silver. For example, on the basis of surface geometry and bond angles,



two species could exist on a catalyst surface at the interatomic cubic lattice spacings of 4.08 Å and at the spacings for closest approach of silver atoms of 2.88 Å. Consequently, equilibria between the silver surface atoms and oxygen gas may be represented by the equations

[8] $$4Ag_{(surface)} + O_{2(g)} = 2Ag_2O_{(complex)},$$

[9] $$2Ag_2O_{(complex)} + O_{2(g)} = 2Ag_2O_{2(complex)}.$$

The observed transitions in the adsorption rates then indicate approximately the termination of process [8] and the commencement of process [9]. In the temperature range of 180° to 220° C. process [8] is rapid whereas process [9] is relatively slow. Both of these processes are rapid at 260° and 300° C. as the transitions were not observed. This postulate of two surface oxygen complexes is only a crude approximation as no significance is given to the influence of variations in the energy properties of different crystalline faces on the kinetics of adsorption, and cognizance is given to only the abrupt changes in the slopes of the Elovich curves. Although these latter abrupt changes occur at surface coverages of approximately 0.5, this does not disprove the proposal by Orzechowski and MacCormack (8) that different kinds of adsorption sites may be associated with different crystalline faces.

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GENERAL DISCUSSION

In an attempt to account for the observed phenomena, it has been postulated that the catalyst surface area may be determined by the Langmuir and B.E.T. gas adsorption methods and that at least two oxygen complexes are formed on the catalyst surface. These postulates lead to a qualitative interpretation of the adsorption kinetics and emphasize opposing views on the chemisorption of oxygen on a silver catalyst. Twigg (13, 14) and Orzechowski and MacCormack (8), in their investigations on the oxidation of ethylene with a silver catalyst, have proposed that only single oxygen adatoms are involved in the adsorption and reaction kinetics and that proposed mechanisms are applicable to homogeneous and heterogeneous surfaces. Twigg assumes that the formation of ethylene oxide and carbon dioxide requires one and two favorably situated oxygen adatoms respectively. Selective poisoning is attributed to an alteration in the configuration of these adatoms. Orzechowski and MacCormack propose that both reactions involve single oxygen adatoms and that different energetic considerations account for the formation of ethylene oxide and carbon dioxide. According to their postulated reaction mechanism, selective poisoning is attributed to preferential poisoning of different crystalline planes or to the formation of impurity centers which influence the activation energies of the several reaction paths. On the other hand, transitions in the adsorption–time curves of this investigation at surface coverages of approximately 0.5 indicate that at least two oxygen complexes occur with one and two oxygen atoms equivalent to two silver atoms. If significance may be attached to the calculated initial rate of adsorption (Table I) for the formation of the latter complex, this rate is of a sufficient magnitude to influence the reaction kinetics of ethylene oxidation. Selective poisoning may then be attributed to the preferential alteration in concentration of these different complexes. This concept of paired oxygen adatoms is different from that proposed by Twigg in that specific account is taken of the surface geometry and complete dissociation of adsorbed molecular oxygen need not occur. This study emphasizes that further experimental data are required for an understanding of the oxygen chemisorption phenomena on silver and that extreme caution must be used in representing the adsorption of oxygen by an analytical rate equation in reaction studies involving a silver catalyst.

ACKNOWLEDGMENTS

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THE REACTION OF DEUTERIUM ATOMS WITH ETHYLENE[1]

By S. Toby[2] and H. I. Schiff

ABSTRACT

Deuterium was dissociated on a hot tungsten filament and the atom concentration measured by isothermal calorimetry. The recombination coefficient of deuterium atoms on a glass surface, coated with metaphosphoric acid, was found to be 3.8×10^{-5}, and similar to that found for hydrogen atoms. The reactions of H-atoms and D-atoms with ethylene were found to be very rapid. The effects on the yields of the products and on their isotopic composition of variations of reactant flow rate, atom concentration, pressure, and atom-detector position were studied. The major products were methanes, ethanes, and ethylenes, with minor amounts of propanes and butanes. The methanes were always highly deuterated while the ethanes were slightly deuterated. A mechanism is proposed to explain the observations based on a flow pattern in the reaction zone. The possibility of differences in the reaction rates of variously deuterated intermediates is also discussed.

INTRODUCTION

The homogeneous reaction between atomic hydrogen and ethylene occurs so rapidly that little is known of the detailed mechanism. Investigations using isotopic hydrogen have been largely qualitative (19, 11). This paper reports an attempt to obtain quantitative data on the products of the reaction between deuterium atoms and ethylene.

EXPERIMENTAL

The method used to produce and detect the deuterium atoms was similar to that used by LeRoy for hydrogen (2, 3, 7). About 2% of the hydrogen or deuterium in a fast flowing gas stream was dissociated into atoms on an electrically heated tungsten filament. The detector was a tightly wound platinum spiral, mounted on a rack which could be moved by a pinion attached to a standard tapered joint. Two teflon gaskets placed on the inner joint prevented the "Apiezon" grease from being squeezed out during rotation and kept the system vacuum-tight. This arrangement had the advantage of eliminating sliding contacts and permitted a constant lead resistance regardless of detector position. The wattage dissipated by the detector was determined from its resistance and the voltage drop across it.

To conserve deuterium, the gas was circulated during an experiment by connecting the vent of the rotary pump through a refrigerated trap to a return line. Blank experiments showed that the exchange between the deuterium and the pump oil was less than 0.5% for six hours' circulation.

The reaction vessel was 22.5 cm. long and 25 mm. in diameter and was coated with metaphosphoric acid. The speed of gas circulation was 1400 $cm.^3$/sec., corresponding to a linear flow rate of 280 cm./sec. through the reaction chamber and a maximum reaction time of 0.08 sec.

[1]*Manuscript received April 3, 1956.*
Contribution from the Department of Chemistry, McGill University, Montreal, Quebec.
[2]*Holder of a National Research Council Studentship, 1953–54, and of a Province of Quebec Scholarship, 1954–55. Present address: Division of Pure Chemistry, National Research Council, Ottawa.*

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Deuterium was prepared from 99.7% deuterium oxide obtained from Atomic Energy of Canada Limited. The deuterium oxide was allowed to react with a carefully degassed mixture of zinc and freshly dehydrated calcium oxide. Deuterium was then evolved at 500°C. (9, 12) by the reaction:

$$Ca(OD)_2 + Zn \rightarrow D_2 + CaZnO_2.$$

The yield of deuterium depended on the rate of heating of the furnace due to the competing reaction:

$$Ca(OD)_2 \rightarrow CaO + D_2O$$

which occurs at temperatures above 350°C. Yields as high as 90% of the theoretical value were obtained with rapid furnace heating. Mass spectral analysis showed the product to be 96% D_2, the remainder being almost entirely HD. Since the reaction under investigation also produced HD as one of the products, additional quantities of D_2 were periodically added to the system to prevent the deuterium content of the circulating gas from dropping below 96%.

The ethylene, obtained from the Ohio Chemical Company, was "trap-to-trap" distilled several times. The center fraction was 99.9% pure, with ethane as the only detectable impurity. About four millimoles of ethylene-d_4 was kindly supplied by Dr. L. C. Leitch of the National Research Council, Ottawa.

Deuterium atoms were allowed to react at room temperature with the ethylene in a conventional fast flow system. The effects of variation of reactant flow rate, atom concentration, deuterium pressure, and atom-detector position were investigated.

The products were condensed in two large, liquid-nitrogen cooled traps, the second of which contained silica gel to retain the methanes. The total "condensible" fraction was first measured volumetrically. The sample was then divided in two and the mass spectrum of one portion determined. Unsaturates were removed from the other portion with acid mercuric sulphate solution (8) and the remaining saturated hydrocarbons analyzed mass spectrometrically. The analysis of the unsaturates was then obtained from the difference between the spectra of the treated and the untreated portions.

Since standard samples of all the deuterated products were not available, approximate procedures were required to interpret the mass spectra. From a mixture known to contain only methane-d_3 and methane-d_4, the probability factors a and b for the ease of removal of H- and D-atoms respectively from the parent molecule were measured for the mass spectrometer used. The values of these parameters for the other methanes were then estimated by linear extrapolation (20), and the mass spectra for all four deuteromethanes were calculated.

The deuteroethanes were analyzed at reduced electron energies (25) using data kindly supplied by Dr. D. P. Stevenson of the Shell Development Company. Analyses were also performed at 70 volts electron energy, using published data (20) for ethane-d_1, -d_2, -d_3, and -d_6, and calculated spectra (24) for ethane-d_4 and -d_5. Since highly deuterated ethanes were present in relatively small amounts, the errors involved in using the calculated spectra were not serious. The agreement between analyses at normal and reduced electron energies was satisfactory.

The deuteroethylenes were analyzed with the aid of published spectra (6). Small quantities of deuteropropanes and deuterobutanes were also found. Their total quantity was estimated from the sum of the ion currents in the "C_2" and "C_4" mass number region.

RESULTS

The Recombination of Hydrogen and Deuterium Atoms

Dingle and LeRoy found (7) that straight lines could be drawn through both first and second order plots for H-atom recombination, and so were unable to assess the relative importance of heterogeneous and homogeneous recombination reactions. We obtained similar results for both H- and D-atoms. Average values for the "pseudo" first order rate constant k', and the "pseudo" second order rate constant k'', for H- and D-atoms are given in Table I. The value for

TABLE I

PSEUDO RATE CONSTANTS FOR H-ATOM AND D-ATOM RECOMBINATION

$k_H' = 3.82 \pm 0.12$ sec.$^{-1}$ $k_D' = 2.77 \pm 0.08$ sec.$^{-1}$	$\frac{k_H'}{k_D'} = 1.38$
$k_H'' = (2.52 \pm 0.06) \times 10^9$ cm.^{3} sec.$^{-1}$ mole^{-1} $k_D'' = (1.66 \pm 0.04) \times 10^9$ cm.^{3} sec.$^{-1}$ mole^{-1}	$\frac{k_H''}{k_D''} = 1.52$

k_H' can be compared with Dingle and LeRoy's value (7) of 4.80 sec.$^{-1}$. The ratio of either the first or the second order rate constants for hydrogen and deuterium should be less sensitive to wall conditions than the individual values, and clearly indicates that H-atoms recombine faster than D-atoms. There are no data with which these ratios can be compared, but Amdur (1) gives a value of 1.36 for k_D'''/k_H''', the ratio of the third order rate constants at 30°C.

The heterogeneous recombination of atoms can also be expressed in terms of a recombination coefficient γ, which may be defined as the ratio of the number of atoms recombining on a surface to the total number striking that surface (21), and is, therefore, independent of the geometry of the apparatus. It can be calculated from the relation

$$\gamma = 2k'r/V$$

where V is the mean atomic velocity and r the radius of the tube. Table II shows the values obtained in this and in other investigations. It will be seen that the values of γ for H- and D-atoms are equal within experimental error. This suggests that any difference between the first order recombination rates is due only to the differences in atomic velocities.

The Reaction of H- and D-Atoms with Ethylene

Preliminary experiments with H-atoms showed that ethane and methane were the main products of the reaction, along with small amounts of propane and butane. The amounts of various products formed in the reaction with D-atoms are given in Table III. Fig. 1 shows the percentage of each product

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TABLE II

RECOMBINATION COEFFICIENT FOR GLASS SURFACE COATED WITH METAPHOSPHORIC ACID

Author	Atoms	$\gamma \times 10^5$	Temp., °C.
Poole (17)	H	3.9	Room temp.
Smith (22)	H	2	15
Dingle and LeRoy (7)	H	4.5	5
This work	H	3.8	25
This work	D	3.9	25

TABLE III

VARIATION WITH REACTANT FLOW

Run	Temp., °C.	Total press., mm. Hg	Partial press. atoms, mm. Hg	Partial press. ethylene, mm. Hg	Percentage products			
					Methanes	Ethanes	*d*-Ethylenes	C_3, C_4
D-21	24.0	1.36	0.0246	0.0182	97.9	2.1	0	0
D-20	23.5	1.37	0.0191	0.025	98.7	1.3	0	0
D-17	23.0	1.34	0.0222	0.0510	84.2	12.6	2.9	0.3
D-27	25.8	1.36	0.0222	0.0599	73.0	—	—	—
D-14	22.0	1.36	0.0199	0.132	70.5	18.5	8.7	2.2
D-12	25.5	1.38	0.0211	0.235	59.2	22.5	14.1	4.2
D-11	25.5	1.41	0.0186	0.239	59.4	23.3	12.7	4.6
D-24	25.0	1.37	0.0216	0.312	53.9	25.0	16.3	4.9
D-18	23.5	1.36	0.0217	0.414	52.4	25.9	19.1	2.6
D-26	25.5	1.36	0.0199	0.491	52.0	26.6	17.9	3.6
D-25	26.5	1.36	0.0241	0.525	51.2	26.7	15.7	6.4
D-15	24.0	1.34	0.0210	0.559	49.4	24.6	20.4	5.6
D-16	23.5	1.35	0.0221	0.625	51.6	24.3	19.6	4.4

as a function of ethylene flow rate normalized for a D-atom flow rate of 1.0 micromoles per second; the amount of each of the deuterated methanes, ethanes, and ethylenes is plotted against reactant flow rate in Figs. 2, 3, and 4 respectively.

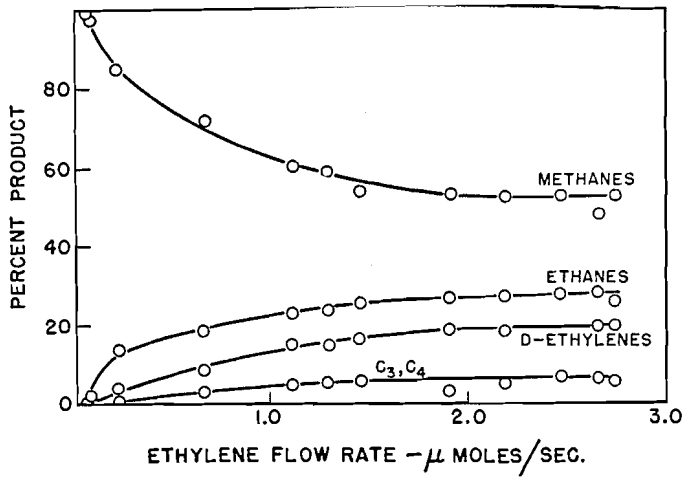

FIG. 1. Variation of total products with ethylene flow rate.

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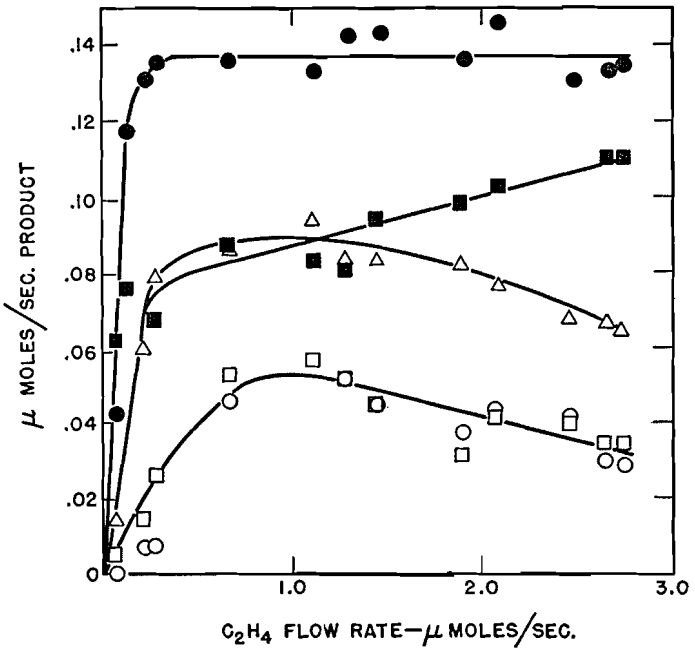

FIG. 2. Variation of methanes with ethylene flow rate.
○, CH_4; □, CH_3D; △, CH_2D_2; ●, CHD_3; ■, CD_4.

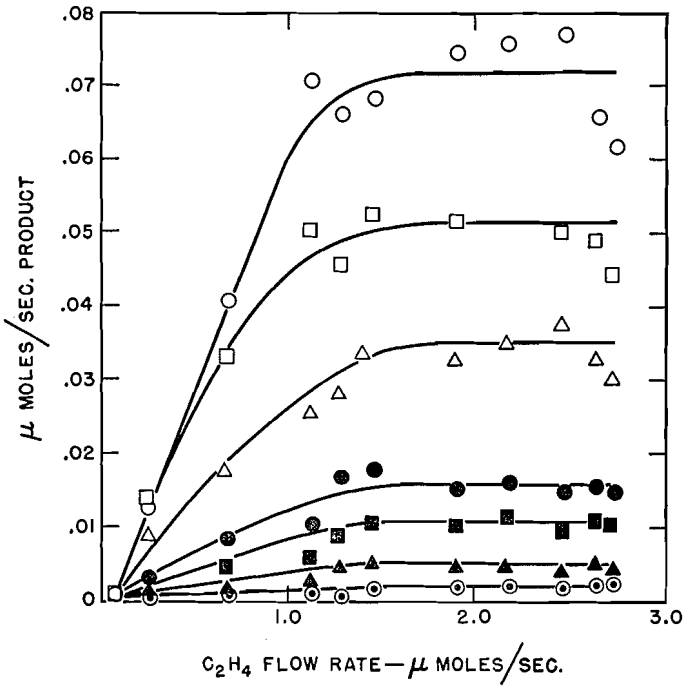

FIG. 3. Variation of ethanes with ethylene flow rate.
○, C_2H_6; □, C_2H_5D; △, $C_2H_4D_2$; ●, $C_2H_3D_3$; ■, $C_2H_2D_4$; ▲, C_2HD_5; ⊙, C_2D_6.

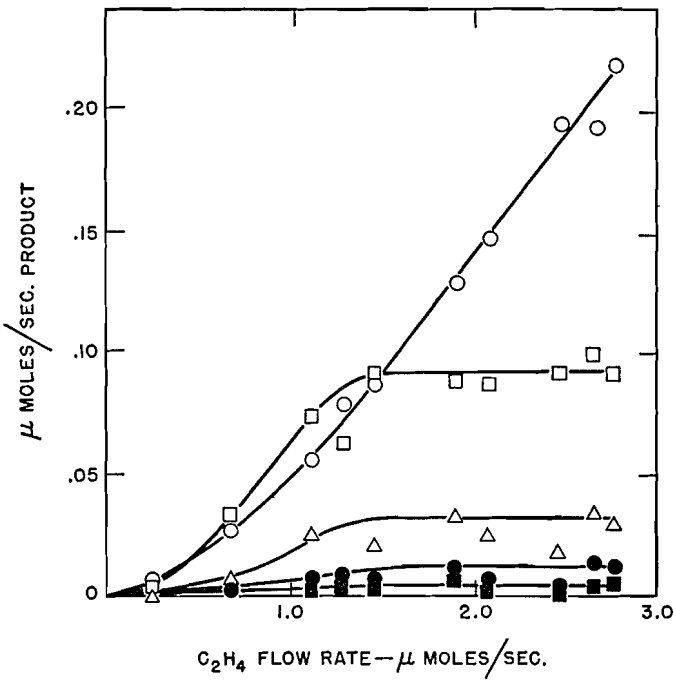

FIG. 4. Variation of ethylenes with ethylene flow rate.
○, $C_2H_4/10$; □, C_2H_3D; △, $C_2H_2D_2$; ●, C_2HD_3; ■, C_2D_4.

The extent of deuteration of any product can be conveniently expressed in terms of the "deuterium number", i.e. the average number of deuterium atoms per molecule of that product. The variation of deuterium number with ethylene flow rate is shown in Fig. 5. The deuterium numbers for the ethylenes do not include unexchanged reactant, and no values are shown at low flow rates, where the amount of unexchanged ethylene was too small for quantitative analysis. In one series of experiments the deuterium pressure was varied while the partial pressure of D-atoms was maintained at 0.028 mm. Hg by controlling the dissociator temperature; the partial pressure of ethylene was 0.017 mm. Hg. The results are plotted along with deuterium numbers in Fig. 6. The deuterium number was pressure dependent only in the case of ethane—with increasing pressure ethane-d_1 became more abundant than ethane-d_0.

Three experiments were performed in which the atom concentration was varied while the deuterium and ethylene pressures were kept constant. Table IV shows the results, and, for comparison, some published data for the reaction of ethylene with H-atoms produced by mercury photosensitization and by the discharge method.

Since all atoms striking the detector are recombined, an attempt was made to alter the reaction time by placing the detector in the reaction chamber during an experiment. Fig. 7 shows the results of a number of experiments in which the detector position was varied from just below the exit tube of the reaction vessel (its normal position during other experiments) to just below the ethylene inlet jet.

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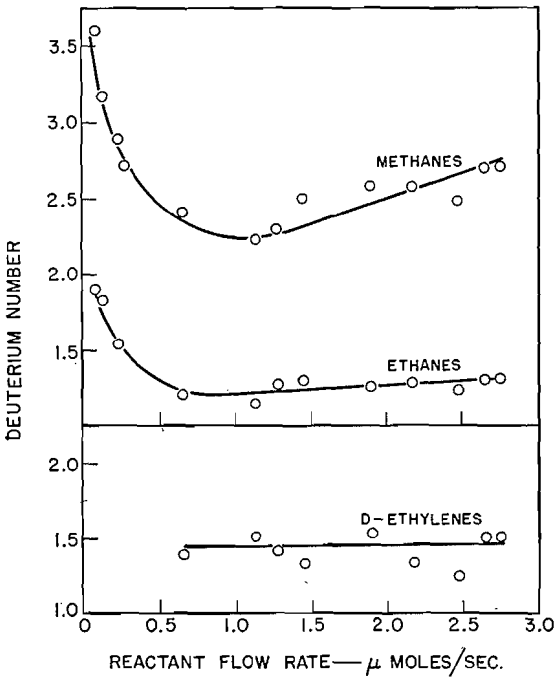

FIG. 5. Variation of deuterium number with ethylene flow rate.

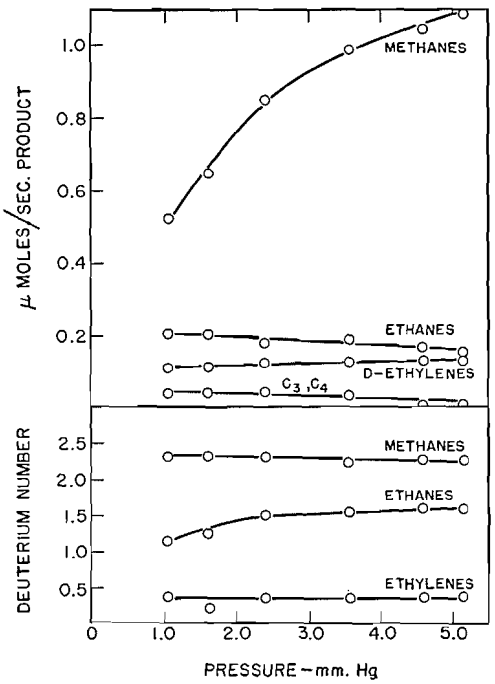

FIG. 6. Variation of products with total pressure.

TABLE IV

VARIATION WITH ATOM CONCENTRATION

Reference	Atoms	Ratio: atoms / reactant	Percentage: Methane	Ethane	Butane
Moore and Taylor (16)	H	*ca.* 10^{-3}	2	14	84
This work	D	0.58	57.6	36.8	5.5[b]
This work	D	1.32	72.2	24.4	3.3[b]
This work	D	2.28	76.0	22.5	1.5[b]
H. I. Schiff (unpublished work)[a]	H	*ca.* 20	92.7	7.3	0

[a]*Traces of acetylene were also found.*
[b]*Includes some propane.*

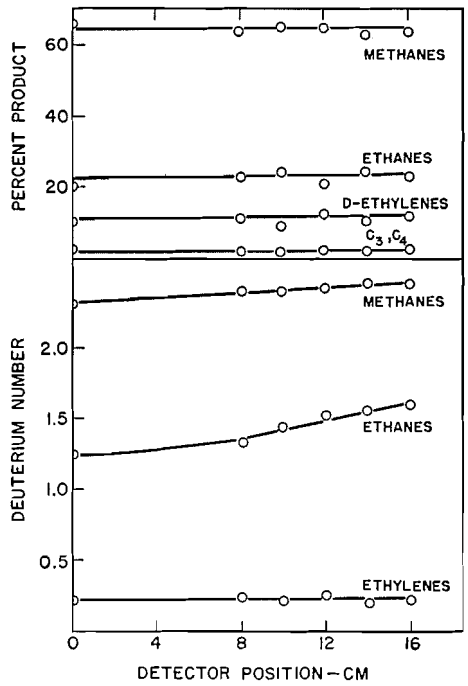

FIG. 7. Variation of products with detector position.

These results indicate that the reaction zone did not extend more than 2 cm. from the inlet jet which corresponds to a reaction time of less than 0.007 sec. The reactions:

$$H + C_2H_4 \rightarrow C_2H_5 , \qquad [1]$$

$$D + C_2H_4 \rightarrow C_2H_4D \qquad [1a]$$

must therefore be very fast and have collision yields greater than 10^{-4}, in agreement with previously reported values (4, 5, 15) for reaction [1].

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DISCUSSION

Perhaps the most unexpected result of this investigation was the production of C_2H_6 and C_2H_5D as the most abundant ethanes in the reaction between D-atoms and ethylene. The amounts of these products were much too large to be accounted for by the hydrogen impurity in the deuterium. Other possible explanations for their occurrence were therefore analyzed. The following possibilities were considered:

(1) *The preferential dissociation of H_2 on the dissociator filament due to its higher dissociation equilibrium constant relative to D_2.* However, calculation showed that this would increase the H-atom concentration by at most 0.1% of the total atom concentration. HD, the largest impurity in the deuterium, dissociates less readily at 2000°A. than does D_2.

(2) *The exchange of D-atoms with the phosphoric acid wall poison.* If the entire increase in HD content observed when the deuterium was circulated for several hours in the absence of ethylene is attributed to this exchange, the maximum production of H-atoms would correspond to less than 1% of the total atom concentration.

(3) *Back diffusion of ethylene to the dissociator.* When helium was substituted for the deuterium 100% recovery of the ethylene was obtained.

(4) *Loss of methane from the silica gel trap and its subsequent dissociation on the tungsten filament.* In view of the excellent mass balances obtained this could not have occurred to any appreciable extent. Moreover, the dissociation of the methanes would not be a good source of H-atoms since they were found to be highly deuterated.

(5) *Heterogeneous reactions occurring on the atom detector.* Experiments with the detector completely removed gave identical results.

(6) *Exchange of the ethanes with the mercuric sulphate solution during the removal of the olefins.* The unsaturates were removed from several samples by reaction with purified bromine; no differences were found.

(7) *Errors in mass spectral analyses due to the lack of standard gases.* Although these errors are difficult to assess quantitatively, comparison of analyses performed both at high and at low electron energies showed that the order of abundance of the deuteroethanes was correct.

Since none of these possibilities is capable of explaining the production of light ethanes, it is reasonable to conclude that these were indeed products of the reaction between D-atoms and ethylene. This can be shown to be stoichiometrically possible. The reactions forming the major products can be formally represented by the equations:

$$\tfrac{1}{2}C_2H_4 + \alpha D \rightarrow C_2D_\alpha H_{4-\alpha} + (\alpha-2)\ H \text{ for methanes,}$$

$$C_2H_4 + \beta D \rightarrow C_2D_\beta H_{4-\beta} + \beta H \text{ for ethylenes, and}$$

$$C_2H_4 + \gamma D \rightarrow C_2D\gamma H_{6-\gamma} + (\gamma-2)H \text{ for ethanes,}$$

where α, β, and γ represent the deuterium numbers of the products. In a typical experiment $\alpha = 2.69$, $\beta = 1.50$, and $\gamma = 1.35$. The yields of the pro-

ducts were 0.377, 0.155, and 0.184 μM./sec. for the methanes, ethylenes, and ethanes respectively. Hence hydrogen atoms could have been generated by the reaction at a rate of $(0.69\times0.377) + (1.50\times1.55) - (0.65\times.184) = 0.37\mu$M./sec. Considerably more H-atoms can therefore be produced in the deuteration of the products than are required for the formation of C_2H_6 and C_2H_5D. This was found to be true in all cases.

However, any mechanism for the reaction must be able to account for these light ethanes along with the other products. In the case of the reaction of H-atoms with ethylene the following elementary reactions may be considered:

$$H + C_2H_4 \rightarrow C_2H_5 \quad [1]$$

$$C_2H_5 \rightarrow C_2H_4 + H \quad [2]$$

$$H + C_2H_5 \rightarrow C_2H_6^* \quad [3]$$

$$C_2H_6^* \rightarrow C_2H_5 + H \quad [4]$$

$$(M+)\ C_2H_6^* \rightarrow C_2H_6\ (+M) \quad [5]$$

$$C_2H_6^* \rightarrow C_2H_4 + H_2 \quad [6]$$

$$C_2H_6^* \rightarrow 2CH_3 \quad [7]$$

$$H + CH_3 \rightarrow CH_4^* \quad [8]$$

$$(M+)\ CH_4^* \rightarrow CH_4\ (+M) \quad [9]$$

$$2CH_3 \rightarrow C_2H_6^* \quad [10]$$

Corresponding reactions can occur with D-atoms.

Formation of Ethylenes

There are several possible explanations for the formation of the deutero-ethylenes. The primary step undoubtedly is

$$D + C_2H_4 \rightarrow C_2H_4D. \quad [1a]$$

Since the deuteroethyl radical probably possesses excess energy it may readily dissociate again:

$$C_2H_4D \rightarrow C_2H_3D + H. \quad [2a]$$

The more highly deuterated ethylenes could be formed from repetition of these two reactions. This mechanism suggests that the yield of deuteroethylenes might be pressure dependent. This was not the case over the pressure range studied.

Alternatively, the deuteroethyl radicals could undergo disproportionation (10). However, the very small butane yields indicated that disproportionation cannot be a major source of deuteroethylene.

The third possibility is that reaction [1*a*] is followed by:

$$D + C_2H_4D \rightarrow C_2H_3D + HD. \quad [6a]$$

However, the repetition of [1*a*] and [6*a*] does not provide an acceptable explanation for the formation of *all* the deuteroethylenes since this sequence does not produce any H-atoms. In some of the experiments the amount of H-atoms which could be derived in the formation of the other products was insufficient to account for the amounts of C_2H_6 and C_2H_5D. This objection

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could be overcome if the deuteroethyl radical first underwent exchange reactions of the type

$$D + C_2H_4D \rightarrow C_2H_3D_2 + H \qquad [4a]$$

prior to forming ethylene by the counterpart of reaction [6*a*]. There is some evidence for [4*a*] from the study of the reaction of D-atoms produced by mercury photosensitization with ethane (23). Deuterobutanes were found which indicated exchange of ethyl radicals before recombination.

Little is known about the likelihood of reaction [6] (or [6*a*]). It is exothermic, but would appear to be less likely than reaction [4], [5], or [7] by the "Principle of Least Motion" (18). However, no unequivocal choice can be made between the first and third explanations for the formation of the deuteroethylenes.

Formation of Methanes and Ethanes

For reasons already indicated, appreciable quantities of ethane could not be formed by disproportionation of ethyl radicals. Moreover, normal disproportionation could not account for the formation of light ethanes. An unlikely "double disproportionation" of the type

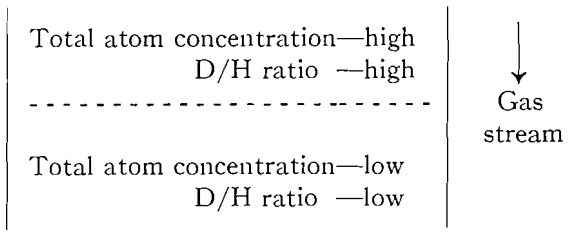
$$C_2H_4D + C_2H_4D \rightarrow C_2H_6 + C_2H_2D_2$$

would be required. The remaining possible sources of ethane are reactions [5] and [10], both of which are preceded by reaction [3]. Methane formation, however, is also preceded by reaction [3]. The problem then arises of accounting for the fact that the methanes were always found to be highly deuterated while the ethanes were only slightly deuterated. A possible explanation can be found by considering the two most likely fates for the methyl radicals in the system:

$$H + CH_3 \rightarrow CH_4 \qquad [11]$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad [12]$$

The distribution of atoms in the reaction zone can be represented diagrammatically as:



The total atom concentration decreases down the reaction tube as a result of both reaction and recombination. But the proportion of H-atoms in the gas stream will increase owing to the exchange of the D-atoms with ethylene and with free radicals.

Reaction [11] will be favored over reaction [12] in the upper part of the reaction zone where the atom concentration is highest. But since this is where the D/H atom ratio is also highest, the methanes will be highly deuterated.

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Under the conditions of low atom concentration at the lower part of the reaction zone reaction [12] will occur more frequently than reaction [11]. But the ratio of H- to D-atoms has increased so that the ethanes will be less deuterated than the methanes.

This picture is in agreement with the observation (Table IV) that the yield of ethane decreases, and the yield of methane increases with increasing atom concentration. The reverse variation of yields with increasing ethylene concentration is likewise consistent with this explanation.

The large increase in methane formation with pressure (Fig. 6) may be attributed to the effect of the deuterium molecule acting as the third body in reaction [9]. The third body requirement is probably more stringent in this reaction than in reaction [10]. The reason for the increase in deuterium number of the ethanes with pressure is not apparent. It conceivably could be due to excited ethyl radicals formed in reaction [1*a*] reacting with D_2.

The experiments in which the atom detector was kept in the reaction chamber also suggested that the methanes are formed very near the ethylene inlet tube while the ethanes are formed lower in the reaction zone. Thus the methanes were unaffected by the presence of the detector while the deuteration of the ethanes was increased.

Although this scheme is qualitatively in accord with the experimental observations, no account has yet been taken of the possibility that the reaction rates of atoms and radicals may depend on their isotopic composition. If the rates were independent of isotopic composition the deuterium distribution for any given product should be controlled by simple probability, and depend solely on the relative amounts of H- and D-atoms available for reaction. For example, the plot between the amount of each deuteroethane against the number of deuterium atoms in the molecule should give a simple probability curve, the maximum of which should correspond to the deuterium number. The heterogeneous reaction between ethylene and molecular deuterium over a heated nickel catalyst (14, 25) produced deuteroethanes which fitted a simple probability curve with a maximum at $C_2H_4D_2$. Keii, however, has pointed out (13) that this agreement may have been largely fortuitous. In the present investigation the less deuterated products were more abundant than would be expected on probability grounds.

Further evidence for the dependence of reaction rate on isotopic constitution was obtained from experiments in which H-atoms were reacted with ethylene-d_4. In the reaction between D-atoms and C_2H_4, the most abundant methane produced was CD_3H. In the reaction between H-atoms and C_2D_4 the most abundant methane was CH_2D_2, and not CDH_3. Similarly, although C_2H_6 was the ethane formed in greatest amount in most of the $D+C_2H_4$ experiments, C_2D_6 was *not* the most abundant ethane formed under similar conditions in the reaction of H with C_2D_4. Owing to the large number of steps required to form some of the products, even a small difference in reaction rates of isotopically different species could account for the differences in the isotopic distributions of the products.

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Because of the complexity of the reaction no decision could be reached as to what extent the deuterium distribution was due to the earlier explanation based on the flow pattern in the reaction zone, and to what extent it was due to differences in reaction rates between variously deuterated intermediates.

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THE REACTIONS OF ACTIVE NITROGEN WITH ALKYL CHLORIDES[1]

By B. Dunford,[2] H. G. V. Evans,[2] and C. A. Winkler

ABSTRACT

The reactions of active nitrogen with methyl, ethyl, vinyl, propyl, and isopropyl chlorides yielded hydrogen cyanide and hydrogen chloride as the main products. Small amounts of cyanogen and a polymer were formed from all the halides, and all except methyl chloride also yielded small amounts of C_2 and C_3 hydrocarbons. The observed changes in amounts of products recovered with different reactant flow rates were characteristic of a fast reaction in which complete consumption of either reactant occurs when the other is present in excess. Mechanisms for the reactions are suggested on the basis that relatively long-lived complexes are formed in the initial attack of a nitrogen atom on the alkyl chloride.

INTRODUCTION

A number of reactions of active nitrogen, produced in a condensed electrical discharge, have been studied in this laboratory. Emphasis has been placed largely, though not exclusively, on the reactions with hydrocarbons (2, 3, 9, 11, 13, 14, 17, 18, 19). Hydrogen cyanide is the main nitrogen-containing product of these reactions, which implies that the reactions with saturated hydrocarbons involve direct attack at a completely shielded carbon atom. They are much faster than would be expected from the principle of least motion enunciated by Rice and Teller (15).

In an attempt to elucidate further the mechanism of the reactions, it appeared desirable to investigate the effect of a chlorine substituent on the reactivity. Accordingly, the reactions of active nitrogen with methyl, ethyl, vinyl, propyl, and isopropyl chlorides have been studied.

EXPERIMENTAL

The reactions were studied with conventional fast-flow techniques (11). Active nitrogen was produced by a condensed discharge and mixed with the halides in a reaction vessel that was sufficiently far from the discharge tube to prevent back diffusion into the discharge. The flow and activation of the nitrogen were kept constant in experiments with a given halide and the effects of change in flow rate of the halide determined. The reaction vessel could be surrounded by a furnace to study the effect of temperature. Condensable products were trapped with the usual arrangement of liquid air traps, and were analyzed by low temperature fractionation (12) and with a mass spectrometer.[3] The hydrogen cyanide, cyanogen, and hydrogen chloride produced in the reactions were estimated by titration (16, 20). The hydrogen produced in the reaction with methyl chloride was determined mass spectrometrically on samples of the gas issuing from the vacuum pump.

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[2]*Holders of National Research Council Studentships and Fellowships.*
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RESULTS

All the reactions produced a peach-colored flame of fairly high luminosity, which was confined to the upper part of the reaction vessel at the higher flow rates.

The main products of all the reactions were hydrogen cyanide and hydrogen chloride; small amounts of cyanogen were also formed. In all the reactions, significant amounts of a brown polymer were formed on the walls of the reaction vessel but not in the traps. This polymer was quite inert, and had properties somewhat resembling those of paracyanogen. Its composition varied appreciably with the different alkyl chlorides and to a lesser extent with different flow rates of a given alkyl chloride. It contained nearly equal amounts of carbon and nitrogen (on a mole basis) together with smaller amounts of chlorine and hydrogen.

The formation of polymer on the walls of the reaction vessel made it difficult to obtain reproducible results at higher flow rates. (The concentration of active nitrogen is very sensitive to wall conditions, and the polymer itself was probably formed by a wall reaction.)

Methyl Chloride

The rates of production of hydrogen cyanide, hydrogen chloride, and hydrogen, and the rate of consumption of methyl chloride, all varied linearly with methyl chloride flow rate up to a flow rate of about 3×10^{-6} mole/sec., and were independent of temperature in this linear region (Fig. 1). In this

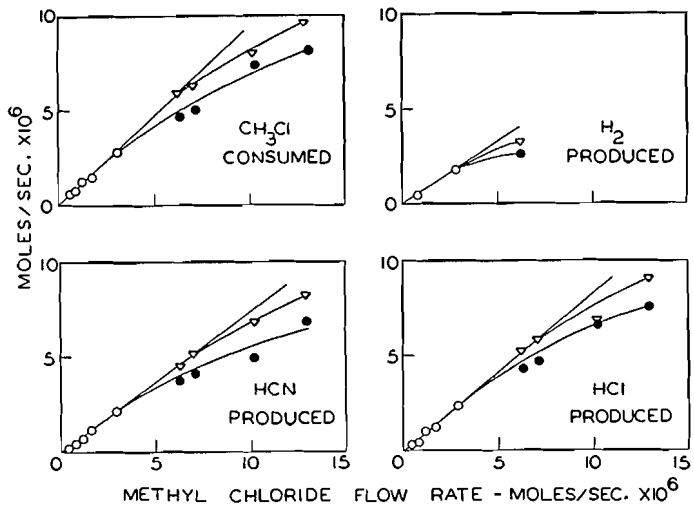

FIG. 1. Relations between methyl chloride flow rate and rates of methyl chloride consumption and product formation.

region, only 89% of the methyl chloride was consumed, independently of flow rate or temperature. At higher flow rates the yields of products approached a limiting value which was the greater, the higher the temperature.

The curves in Fig. 1 have only qualitative significance, since deposition of polymer changed the surface condition of the thermocouple wells at the center

and top of the reaction vessel and the thermocouple readings were therefore only a rough measure of the reaction temperature. Quite marked changes in the readings were observed both during an experiment and in successive experiments. In addition, the reaction was sufficiently exothermic to create marked temperature gradients in the reaction vessel. The temperatures at the center of the reaction vessel have therefore been recorded, rather arbitrarily, as "low" and "high" corresponding roughly to 100° and 300°C. respectively.

The amount of cyanogen formed was quite erratic, but it was always less than 3% of the methyl chloride consumed. A careful search failed to reveal the presence of any cyanogen chloride, methane, or ethane in the products.

Ethyl, Vinyl, and Propyl Chlorides

In these reactions, small amounts of hydrocarbons were formed as secondary products. Vinyl chloride gave only acetylene, ethyl chloride gave a mixture of C_2 hydrocarbons, and the propyl chlorides gave mixtures of C_2 and C_3 hydrocarbons. The composition of these products did not change significantly with flow rate in the limited range where samples sufficiently large for analysis could be recovered. Typical values are: for ethyl chloride, 94% ethylene, 5% acetylene, 1% ethane; for *n*-propyl chloride, 34% propylene, 41% ethylene, 17% acetylene, 6% propane, 2% ethane; for isopropyl chloride, 42% propylene, 33% ethylene, 18% acetylene, 6% propane, 1% ethane.

Figs. 2 and 3 show the changes in amounts of products recovered with different reactant flow rates. The different limiting yields with the various reactants may be attributed to changes in operating conditions, particularly the wall conditions in the reaction vessel. The shape of the curves for hydrogen cyanide production from the alkyl halides is quite similar to that of the analogous curves for the olefins (9, 17, 18), and is typical of a fast reaction in which there is complete consumption of either reactant when the other is present in excess. Although the break in the curve for hydrogen cyanide production is not as sharp for vinyl chloride as for the other chlorides, the general character of the reaction and comparison with the similar behavior of acetylene (19) leave no doubt that the reaction of active nitrogen with vinyl chloride is fast.

The reactions of the higher halides were even more exothermic than the reaction with methyl chloride, and the difficulties of temperature measurement were aggravated to such an extent that it was not possible to obtain meaningful results. A few experiments with ethyl chloride in a heated reaction vessel indicated that the yields of products were independent of temperature within experimental error.

DISCUSSION

There is some evidence that active nitrogen contains more than one chemically reactive species (7, 8, 14). However, considerations outlined in a further paper (4) suggest that one species, probably atomic nitrogen, is responsible for most of the reaction observed with the hydrocarbons and related compounds, and it is on this basis that the present results will be discussed.

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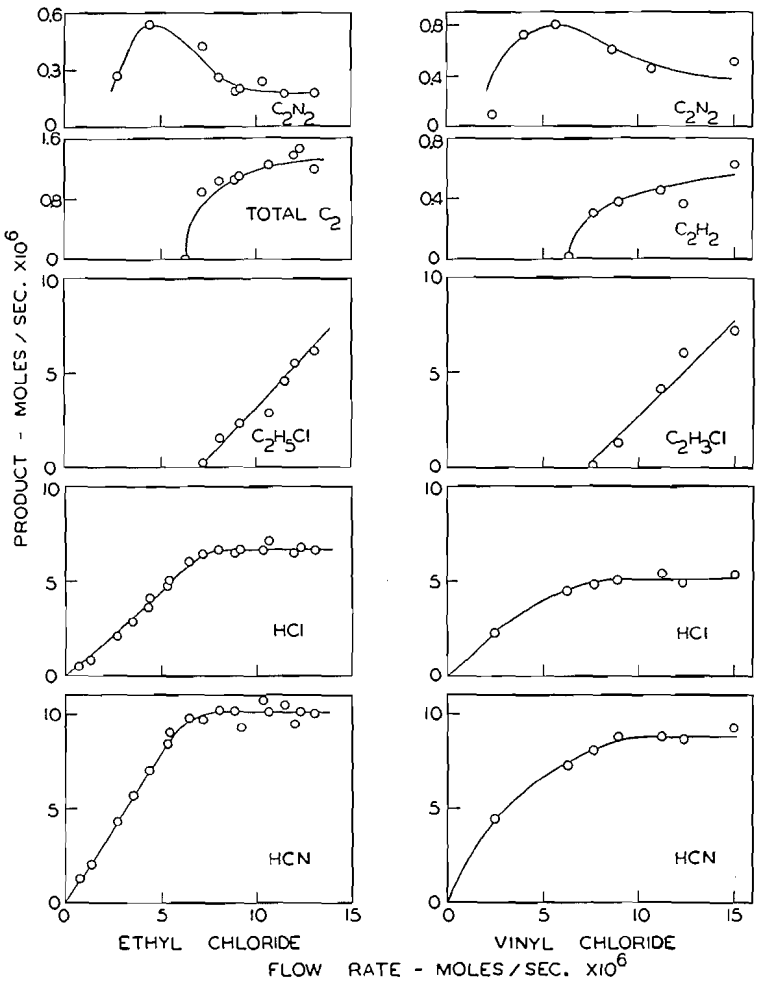

FIG. 2. Relations between rates of product formation and flow rates of ethyl and vinyl chlorides.

The observed initial linear variation in yield of hydrogen cyanide with methyl chloride flow rate, and its temperature independence, appear to be possible only for a fast reaction. It can be estimated from the experimental conditions that this behavior must correspond to a collision yield greater than about 5×10^{-5}. Similar results would probably be obtained for the higher halides, but the low flow rate region was not investigated as thoroughly for these reactions.

The recovery of methyl chloride at low flow rates might be attributed mainly to decomposition of nitrogen atom – methyl chloride complexes back to methyl chloride and nitrogen on the cold surface of the trap, although some channelling of methyl chloride in the flow through the reaction vessel might have occurred. Competition between a fast reaction of nitrogen atoms with methyl chloride and fast recombination of nitrogen atoms catalyzed by methyl

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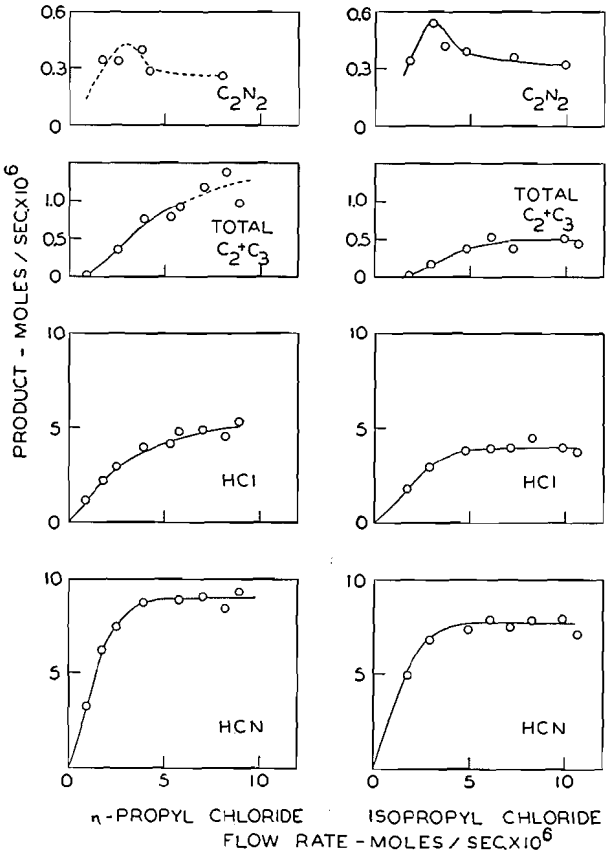

FIG. 3. Relations between rates of product formation and flow rates of propyl and isopropyl chlorides.

chloride or one of the reaction products can explain the observation that the yields were independent of temperature at low flow rates and increased with temperature at high flow rates. Similar, but more pronounced effects have been found in the reaction of methyl cyanide with active nitrogen where the temperature measurements were more trustworthy (5). A mathematical treatment of the problem is in preparation.

The features of the methyl chloride reaction outlined above suggest that a relatively long-lived methyl chloride – nitrogen atom complex was formed. The assumption that such complexes are formed in the reactions of the higher halides appears to be necessary to explain the formation of the secondary products. Further, the close similarity of the reactions of the higher halides to those of the unsaturated hydrocarbons suggests the possibility that hydrogen chloride is eliminated during formation of the complex, to yield a nitrogen atom complex with the corresponding unsaturated hydrocarbon. This is more fully discussed in the subsequent paper (4) on the basis of which it is possible to suggest the following mechanisms for the formation of the products obtained from the various active nitrogen – alkyl chloride reactions:

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Methyl Chloride

$$CH_3Cl + N \rightarrow N.CH_3Cl \rightarrow HCN + HCl + H$$
$$H + H \rightarrow H_2$$

Ethyl Chloride

$$C_2H_5Cl + N \rightarrow N.C_2H_5Cl \rightarrow HCl + N.C_2H_4$$
$$N.C_2H_4 \rightarrow HCN + CH_3$$
$$CH_3 + N \rightarrow HCN + 2H$$
$$N + N.C_2H_4 \rightarrow N_2 + C_2H_4$$
$$N + N.C_2H_4 \rightarrow N_2 + C_2H_4^* \text{ (possibly } \dot{C}H_2\dot{C}H_2^*)$$
$$C_2H_4^* \rightarrow H_2 + C_2H_2^* \text{ (possibly } \dot{C}H{=}\dot{C}H^*)$$

Propyl Chloride

$$C_3H_7Cl + N \rightarrow N.C_3H_7Cl \rightarrow HCl + N.C_3H_6$$
$$N.C_3H_6 \rightarrow HCN + C_2H_4 + H$$
$$N.C_3H_6 \rightarrow N_2 + C_3H_6$$
$$N + N.C_3H_6 \rightarrow N_2 + C_3H_6^* \text{ (possibly } CH_3{-}\dot{C}H{-}\dot{C}H_2^*)$$
$$C_3H_6^* \rightarrow CH_3{-}CH^*{:} + CH_2$$
$$CH_3{-}CH^*{:} \rightarrow C_2H_4$$
$$CH_3{-}CH^*{:} \rightarrow C_2H_2 + H_2$$

Vinyl Chloride

$$CH_2CHCl + N \rightarrow N.CH_2CHCl \rightarrow HCl + N.C_2H_2$$
$$N.C_2H_2 + N \rightarrow N_2 + C_2H_2$$
$$N + N.C_2H_2 \rightarrow 2HCN$$

It will be noted that the formation of the secondary hydrocarbon products is accompanied by recombination of two nitrogen atoms. This recombination appears to be the only source of sufficient energy to form these products and, for their formation in significant amounts, it is obviously necessary that a relatively long-lived complex should be formed. Thus, the higher halides might be expected to show the same change in yields with temperature at higher flow rates that was observed for methyl chloride. In spite of experimental difficulties, there was some indication that the effect was less marked for the higher halides. This might indicate a lower activation energy for these reactions. On the other hand, the spontaneous decomposition of complexes containing more than one carbon atom would make available carbon-containing intermediates that should react very rapidly with nitrogen atoms (1) and the direct reaction should be favored over the recombination.

The cyanogen produced in the alkyl chloride reactions was probably formed by the combination of two cyanogen radicals. The recombination of two nitrogen atoms makes available some 225 kcal. of energy, and there is a quite high probability that a substantial part of this energy is transferred from the newly forming N_2 molecule to the internal degrees of freedom of the rest of the complex (4). This can bring about dissociation into very reactive fragments. For methyl chloride, for example, reactions of the following type are all exothermic:

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$$N + N.CH_3Cl \rightarrow N_2 + CH_2Cl + H$$
$$N + N.CH_3Cl \rightarrow N_2 + HCl + CH + H_2$$
$$N + N.CH_3Cl \rightarrow N_2 + CH_2 + H + Cl.$$

It seems rather likely that cyanogen radicals will be formed by reaction of such fragments with still another nitrogen atom, e.g.

$$N + CH_2 \rightarrow CN + H_2$$
$$N + CH \rightarrow CN + H.$$

These reactions are sufficiently exothermic to give the electronically excited cyanogen radicals that are responsible for emission of the reaction flames (4). For the higher halides it is possible that some cyanogen was formed directly by such reactions as

$$N + N.C_2H_4 \rightarrow (CN)_2 + 2H_2.$$

However, this type of reaction involves a great deal of rearrangement, and more likely are reactions such as

$$N + N.C_2H_4 \rightarrow N + 2CH_2$$
$$N + CH_2 \rightarrow CN + H_2$$
$$2CN \rightarrow (CN)_2.$$

The fact that cyanogen production passes through a maximum at low chloride flow rates seems to be good evidence that more than two atoms of nitrogen are involved in its formation. If only two nitrogen atoms were involved, cyanogen production from the ethyl chloride reaction should be similar to the ethylene production, at least at high flow rates where the amount of ethylene reacting with nitrogen atoms can be neglected.

According to the mechanism suggested above, the production of unsaturated hydrocarbons should pass through a maximum as the chloride flow rate is increased. The chloride flow rate at which this maximum should occur will depend upon the relative rates of the reactions of the chlorides and the unsaturated hydrocarbons with nitrogen atoms. Apparently, the maximum yields were not attained in the region studied and this, together with the observation that little or no unsaturated hydrocarbons were recovered at low flow rates, gives some indication that nitrogen atoms react faster with the unsaturated hydrocarbons than with the alkyl chlorides.

The presence of highly reactive intermediate species in the reactions of the halides with nitrogen atoms, and particularly the presence of free CN radicals, probably accounts for the formation of polymer by a wall reaction involving mainly CN radicals with smaller amounts of the other intermediates. This would mean that recombination of two nitrogen atoms was necessary for polymer formation, in agreement with the observation that the polymer was formed near the top of the reaction vessel, especially at higher flow rates. It would also account for the differences in composition of the polymer from the different reactions.

The mechanisms outlined above involve production of hydrogen atoms, and the small amounts of saturated hydrocarbons formed in the reactions of the higher halides probably resulted mainly from hydrogenation of the correspond-

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ing olefin. Failure to detect methane as a product indicates that the concentration of atomic hydrogen was low in all the reactions. Hydrogen chloride (10) and methyl cyanide (6) are efficient recombination catalysts for hydrogen atoms. It seems quite possible that alkyl halides would behave like methyl cyanide in this respect, and in any event there was probably enough hydrogen chloride formed in the reactions to keep the concentration of hydrogen atoms at a low value.

The occurrence of secondary reactions involving more than one nitrogen atom makes it necessary to be cautious in drawing conclusions about the rate of the primary reaction, particularly since many of the products of these secondary reactions are known to react fast with nitrogen atoms. However, it seems likely (4) that the main energy barrier for the reactions is surmounted when the complex is formed. This conclusion would have to be modified if the secondary reactions formed products capable of reacting with alkyl chlorides to set up a chain reaction. For the methyl chloride reaction, hydrogen and chlorine atoms are possible chain carriers. However, the absence of any detectable amounts of methane, ethane, chlorine, cyanogen chloride, or ethylene chloride in the products makes it seem unlikely that there was an important contribution from chain reactions carried by hydrogen or chlorine atoms. It is possible to write a reaction scheme for a chain carried by CN radicals:

$$N + CH_3Cl \rightarrow N.CH_3Cl$$
$$N + N.CH_3Cl \rightarrow N_2 + CH_2Cl + H$$
$$N + CH_2Cl \rightarrow CN + HCl + H$$
$$CN + CH_3Cl \rightarrow HCN + CH_2Cl.$$

The third reaction is exothermic and should be very fast (4), but it is doubtful that the last reaction would be fast enough to be effective as a chain carrier. Absence of a significant contribution from a chain reaction is also indicated by the reactions of the higher halides. In these, the recovery of unsaturated hydrocarbons with the same number of carbon atoms as the parent halide provides good evidence that the main path of the reaction was not hydrogen or chlorine atom abstraction followed by nitrogen atom attack on the resulting radical.

It appears probable, from the foregoing discussion, that the reactions of nitrogen atoms with alkyl chlorides involve direct attack at a shielded carbon atom without requiring a high activation energy.

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THE VIBRATIONAL SPECTRA OF ACETALDEHYDE AND ACETALDEHYDE-d_1 [1]

By J. C. Evans[2] and H. J. Bernstein

ABSTRACT

The Raman spectra of liquid CH_3CHO and CH_3CDO were obtained photoelectrically and depolarization ratios measured. Infrared spectra of the vapors and solids were also obtained. A vibrational assignment is given and the spectra correlated. The vibrational spectra of the acetyl halides reported in the literature are also correlated.

Several infrared and Raman investigations of acetaldehyde and acetaldehyde-d_4 have been made but complete agreement as to the vibrational assignments has not been reached (3, 4, 6, 7, 8, 9, 12, 14). Pitzer and Weltner's reassignment (9) is consistent with the thermodynamic data but has not been definitely established. The reported depolarization ratios of some of the Raman bands (4) are inconsistent with this assignment and, recently, a different assignment for the low lying bands has been proposed (6).

The most promising source of further relevant information seemed to be the vibrational spectrum of acetaldehyde-d_1 (CH_3CDO) and an investigation of the Raman and infrared spectra of this molecule has been made. The Raman spectrum in the liquid phase and the infrared spectra in the vapor and solid phases have been examined. Similar studies were made on acetaldehyde.

The vibrational assignment for acetaldehyde which is indicated by these results is very similar to that made by Pitzer and Weltner; the revisions are mainly in the higher wave number region and have negligible effect upon the calculated thermodynamic functions.

The spectra of the related molecules, the acetyl halides, may now be correlated with some success.

EXPERIMENTAL

Acetaldehyde (Eastman Kodak) was refractionated. Acetaldehyde-d_1 was prepared and fractionally distilled by Dr. L. C. Leitch.

A White grating spectrometer with photoelectric recording (16) was used to obtain the Raman spectra of the two compounds in the liquid phase. Depolarization ratios were measured (2) and corrected for convergence error (10). The infrared spectra were obtained with a Perkin Elmer Model 12C (double pass) spectrometer with LiF, CaF_2, NaCl, and KBr optics. A low temperature cell of the type described by Wagner and Hornig (15) was used to measure the infrared spectra of the solids.

The spectra are illustrated in Figs. 1 to 4 and the data are collected in Tables I and II.

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[2]*National Research Council Postdoctorate Research Fellow 1953–55.*

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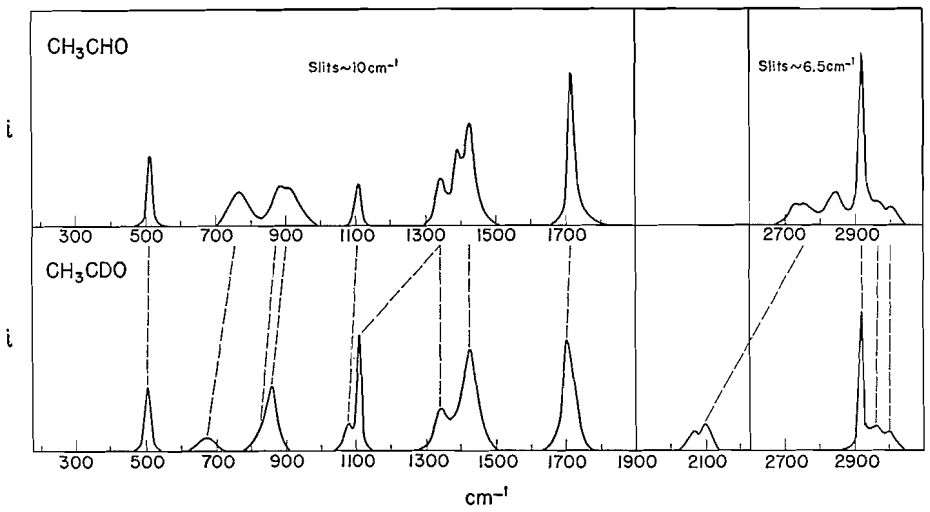

FIG. 1. The Raman spectra of CH_3CHO and CH_3CDO in the liquid phase. Intensity scales are arbitrary and are not strictly comparable. Above 1900 cm.$^{-1}$, the intensity scales are reduced by a factor of five. Excitation by 4358 Å Hg.

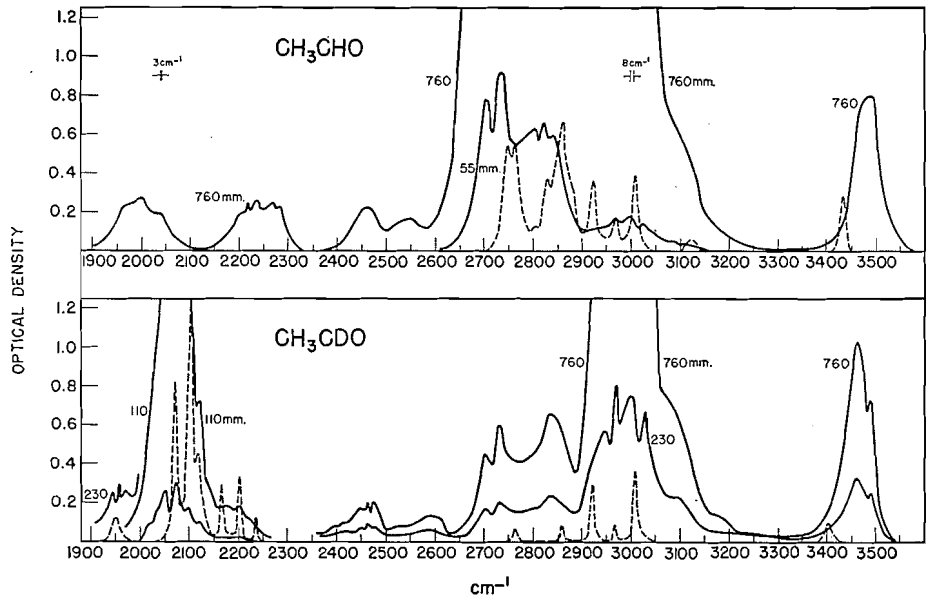

FIG. 2. The infrared spectra of CH_3CHO and CH_3CDO, 3600-1900 cm.$^{-1}$.
Vapor spectra: cell length = 10 cm.; temperature 20° C. Vapor pressures are given on the curves.
Solid spectra: broken lines. Films of unknown thicknesses at −180° C.

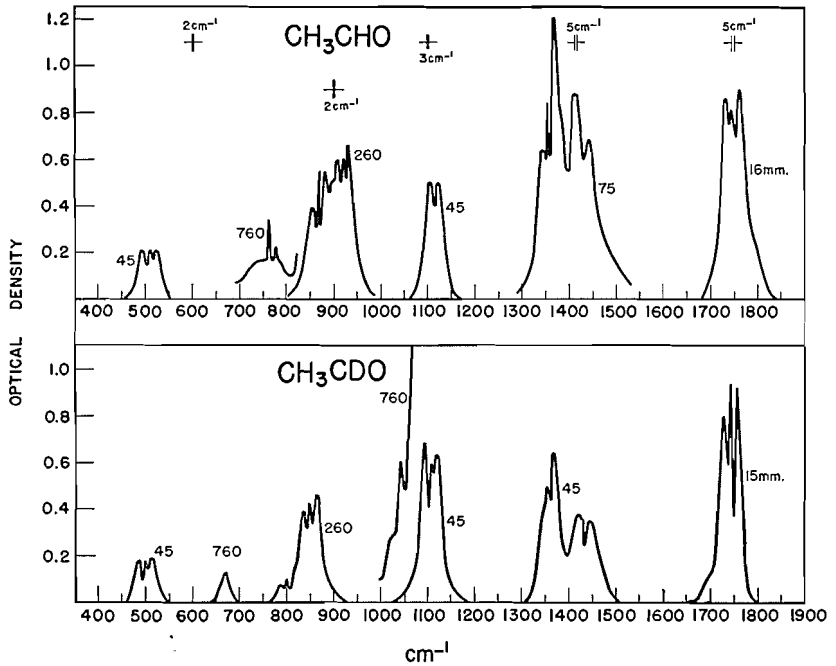

FIG. 3. The infrared spectra of CH_3CHO and CH_3CDO. Vapor spectra between 1900 and 450 cm.$^{-1}$. Vapor pressures are given on the curves. 10 cm. cell at 20° C.

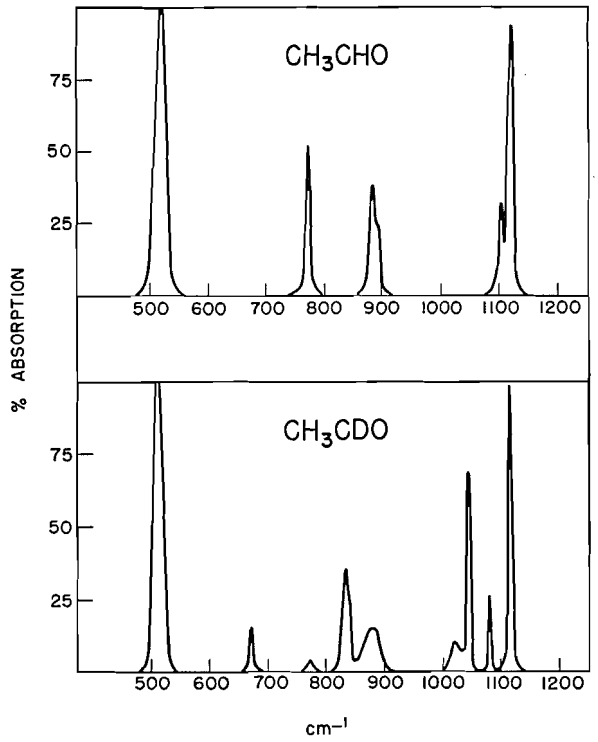

FIG. 4. The infrared spectra of CH_3CHO and CH_3CDO. Solid spectra 1200-450 cm.$^{-1}$. Films of unknown thickness at −180° C.

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TABLE I
CH_3CHO

Infrared		Raman		Assignment
Vapor	Solid	liquid	$\rho_{corr.}$	
3485	3432			$2\times1743 = 3486$ (A')
~3120	3125			$1743+1400 = 3143$ (A')
3024	3007	3001	0.87	a''; $\nu(CH_3)$
2996				
2967	2967	2964	~0.76	a' ; $\nu(CH_3)$
	2920	2917	0.10	a' ; $\nu(CH_3)$
2840	2876			a' ; $\nu(CH)$
2822	2859	2843	0.22	
2804	2827 sh			$2\times1400 = 2800$ (A')
				$2\times1352 = 2704$ (A')
2736	2762	2751	0.31	and other combinations of
2704	2749	2731	0.36	1352, 1400, and 1430 cm.$^{-1}$
2550				$1743+(830) = 2573$ (A'')
2464				$1352+1111 = 2463$ (A')
2282				$919+1352 = 2271$ (A')
2268				
2236				
2218				$2\times1111 = 2222$ (A')
2206				
2040				$919+1111 = 2030$ (A')
2000				
1960				
1790 sh				$2\times919 = 1838$ (A')
		~1740 sh	?	$919+(830)$
1761				
1743		1714	0.33	a'; $\nu(C{=}O)$
1732				
1441	1422	1426	~0.8	a' and a''; def. (CH_3)
~1420				
~1410				
	~1390	1391	~0.65	a'; C—H rocking
~1390				
1369				
1352	1349	1342	~0.8	a'; def. (CH_3)
1341				
1122	1120	1109	0.34	a'; ν(C—C)
1104				
	1103			888+tors. (~230 cm.$^{-1}$)
930				
919	888 sh	911	0.45	a'; CH_3 rocking
909				
880				
867	883	885	p. or dp. (?)	a''; CH_3 rocking
853				
777				A''; 509+tors. (?)
763	772	767	0.87	a''; C—H wagging
521				
509	517	512	0.40	a'; δC—C=O
493				

In Tables I and II estimated positions are used for the coupled modes in determining the wave numbers of overtones and combination tones. These estimated values are bracketed.

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TABLE II

CH_3CDO

Infrared		Raman		Assignment
Vapor	Solid	liquid	$\rho_{corr.}$	
3490				
	3405			$2\times1743 = 3486$ (A')
3462				
3173				$1743+1431 = 3174$ (A' and/or A'')
3096				$1743+1353 = 3096$ (A')
3028	3008	2998	~0.86	a''; $\nu(CH_3)$
3000				
2970	2968	2965	~0.76	a' ; $\nu(CH_3)$
2946				
	2921	2917	0.13	a' ; $\nu(CH_3)$
2840	2859			$2\times1431 = 2862$ (A' and/or A'')
2733	2764			$1353+1431 = 2784$ (A' and/or A'')
2704				$2\times1353 = 2706$ (A')
2600				$1743+(890) = 2633$ (A')
2528				$1431+1109 = 2540$ (A', A'')
2476				
2465				$1353+1109 = 2462$ (A')
2450				
2416				
				$1743+668 = 2411$ (A'')
2400				
2222	2234			$1431+802 = 2233$ (A' and/or A'')
2200	2202			$2\times1109 = 2218$ (A')
2175	2165			$1346+833 = 2179$ (A'')
2148				$(1040)+1109 = 2149$ (A')
	2117 sh			$1116+2\times513 = 2139$ (A')
2120				Fermi doublet
	2103	2097	0.35	
2096				$2\times(1040)$
2071				a'; ν(C—D)
	2071	2069	0.36	
2050				
2036				
				$1353+668 = 2021$ (A'')
2018				
1970				
1958	1950			$1109+(890) = 1999$ (A')
1945				
		1714 sh	?	$(810)+(890) = 1700$ (A'')
1757				
1743	1690	1702	0.21	a'; ν(C═O)
1730				
1442				
	1417	1426	0.80	a'; a''; CH_3 def.
1420				
1366				
1353	1346	1343	0.68	a'; CH_3 def.
~1345				
1244 v.v.w.				$2\times668 = 1236$ (A')
1192 v.v.w.				?
1118				
1109	1116	1111	0.12	a'; C—D rocking
1094				
Overlapped	1081	1080	0.50	a'; ν(C—C)
1043 v.w.	1040			833+tors. (?)
1025				
	1023			$2\times513 = 1026$ (A')

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TABLE II (*Concluded*)

Infrared		Raman		Assignment
Vapor	Solid	liquid	$\rho_{corr.}$	
924 v.v.w. 913				668+tors. (?)
865 849 837	~880	858	0.46	a'; CH_3 rocking
816 802 799	833	~820 (overlapped)	?	a''; CH_3 rocking
	770			?
668	672	674	~0.86	a''; C—D wagging
513 500 487	513	505	0.36	a'; δC—C=O

DISCUSSION OF RESULTS

Following previous authors, symmetry C_s is assumed for both molecules. Each molecule should have ten a' and five a'' fundamental modes of vibration. All modes should be infrared and Raman active, the Raman bands arising from the a' modes being polarized and those from the a'' modes being depolarized. Moments of inertia were calculated* and the structures expected for the principal types of infrared bands were determined according to Badger and Zumwalt (1), some extrapolation of their results being necessary in this case. The a'' modes should give rise to bands with strong central peaks (C type) while the a' modes should give rise to hybrid bands, i.e. bands which consist of doublets with or without a weak central peak. The separation of the doublets was calculated, using the symmetric rotator formulae (5), to be ~27–28 cm.$^{-1}$ for both CH_3CHO and CH_3CDO. The symmetric top approximation is not a very good one in these cases but several doublets of approximately this separation were observed.

The C—H Stretching Modes

Comparison of the spectra of the two molecules in the 3000 cm.$^{-1}$ region gives immediately those bands which arise from the aldehyde CH group and the overtone and combination tone levels which are in Fermi resonance with it. The infrared spectra of the vapors show overlapping bands which are not readily identified individually but the solid spectra and the Raman spectra of the liquids are more clearly resolved. The depolarization ratios in the Raman spectra distinguish between the a' and a'' asymmetric CH_3 stretching modes at 2965 and 3001 cm.$^{-1}$ respectively. Previous assignments in this region are markedly different.

**Dimensions used in calculating the moments of inertia were: C—H=C—D = 1.09 Å; C—C = 1.50 Å; C=O = 1.22 Å; angle CHO = 120°; CH_3 angles tetrahedral (13).*

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C—D Stretching Mode

Strong Fermi resonance between the fundamental and an overtone or combination tone is evident from the appearance of two almost equally intense, similarly polarized bands in the Raman spectrum of liquid CH_3CDO. The infrared spectrum of the solid shows similar features with further overtone or combination bands in the vicinity, but a reduction in the extent of the resonance is indicated by the infrared spectrum of the vapor. A band with doublet structure of separation $\sim$21 cm.$^{-1}$ is the pronounced feature present. The identity of the level which resonates with the fundamental ν(CD) will be discussed in conjunction with the assignment of the modes in the 1000 cm.$^{-1}$ region.

Region below 1800 cm.$^{-1}$

The new data did not warrant any major change in Pitzer and Weltner's assignment of the fundamentals which lie in this region, but they did provide support in some instances and confirmation in others. Fig. 1, giving the Raman spectra of the two liquids, shows that the in-plane aldehyde C—H rocking mode is at 1391 cm.$^{-1}$, and in CH_3CDO it is at 1111 cm.$^{-1}$. In the infrared spectra of the vapors, the bands overlap but it is apparent that the most pronounced difference between the two spectra in the CH_3 deformation region is at $\sim$1410 cm.$^{-1}$. The aldehyde group CH rocking mode is therefore identified.

The out-of-plane wagging modes of the aldehyde C—H and C—D groups may confidently be assigned to the two depolarized Raman bands at 767 and 674 cm.$^{-1}$ respectively. Both bands are very weak in the infrared but both have the expected *C* type structure. It has been suggested recently that this C—H mode in CH_3CHO coincides with the skeletal bending mode near 500 cm.$^{-1}$, part of the evidence for this being the reported depolarization ratio of 6/7 for the Raman band (4). However, this band, which was hardly affected by deuterium substitution at the aldehyde C—H group, was observed here to be polarized in both molecules.

The remaining bands, in the 800–1200 cm.$^{-1}$ region, may be readily correlated in the two molecules but for an understanding of the differences between the spectra it is necessary to postulate coupling of the various vibrational modes.

The *C* type bands at 867 cm.$^{-1}$ in CH_3CHO and at 802 cm.$^{-1}$ in CH_3CDO arise from the one a'' mode which is expected in this region, a CH_3 rocking mode. The corresponding Raman bands should be depolarized but in both cases overlapping with adjacent polarized bands prevented this from being confirmed. The unexpectedly large difference in position of this band in CH_3CHO and CH_3CDO ($\sim$65 cm.$^{-1}$) may be explained in the following manner. In CH_3CHO coupling of the two a'' modes, C—H wagging and CH_3 rocking, which are both close to 800 cm.$^{-1}$, forces the two energy levels apart, one increasing in wave number and the other decreasing. In CH_3CDO the coupling is removed and the apparent shift in the CH_3 rocking mode is appreciably more than the shift expected for an uncoupled mode of this kind. Two

modes remain to be assigned in this region, the C—C stretching and the CH_3 rocking modes, both being a' modes. The situation is further complicated in CH_3CDO by the presence of the a' mode, C—D rocking in this region. In CH_3CHO there are two bands, the higher of which at 1109 cm.$^{-1}$ in the Raman spectrum has been assigned by Pitzer and Weltner to the ν(C—C) mode. This high value was favored because of the measured, short C—C bond (13). The other band, at 911 cm.$^{-1}$ (Raman), is then the CH_3 rocking mode.

At first sight, comparison of the spectra of CH_3CHO and CH_3CDO would indicate a reversal of this assignment since the band at 911 cm.$^{-1}$ in CH_3CHO is at 858 cm.$^{-1}$ in CH_3CDO and the band at 1109 cm.$^{-1}$ in CH_3CHO is at 1080 cm.$^{-1}$ in CH_3CDO, that is, we have the surprising result that deuterium substitution has a greater effect upon the CH_3 rocking mode than upon the C—C stretching mode. However, if because of this apparent anomaly, the assignments were reversed, a further important feature of the spectrum of CH_3CDO, the Fermi doublet at ~2080 cm.$^{-1}$, would still remain unexplained. Since it is not possible to find a suitable overtone or combination of the observed bands in CH_3CDO to account for this doublet, it must be assumed that the overtone of a perturbed fundamental is involved. A plausible suggestion is that the 1109 cm.$^{-1}$ band in CH_3CHO arises from ν(C—C) and that on deuterium substitution it would fall to ~1050 cm.$^{-1}$. However, interaction with the a' CH_3 rocking mode gives rise to two levels at 1080 cm.$^{-1}$ and 858 cm.$^{-1}$, and thus the unexpectedly large change in the CH_3 rocking mode is explained. An equally plausible explanation is that the main interaction is between the C—D rocking mode and the CH_3 rocking mode, the band at ~2080 cm.$^{-1}$ being then the first overtone of the C—D rocking mode, which, if uncoupled, would lie at ~1050 cm.$^{-1}$. It is noteworthy that in CH_3CHO, ν(C—H) is in strong Fermi resonance with two overtones or combination bands, one of which is very probably the overtone of the C—H rocking mode. However, the assignments of overtone and combination bands in Table II are based on the first explanation, although no serious difficulty would be encountered in using the alternative explanation.

Product rule ratios were calculated* assuming negligible interaction between the torsional modes and the other a'' modes. Theoretical and observed

TABLE III

Species	Theoretical ratio	Observed ratio
a'	1.91	1.89
a''	1.20	1.22*

*The observed ratio is, of course, dependent upon the uncertainties in estimating the position of the unresolved band 825 cm.$^{-1}$

*Moments of inertia used were:
CH_3CHO: $I_A = 16.6$; $I_B = 78.8$; $I_C = 90.1\times10^{-40}$ gm. cm.^{2}
CH_3CDO: $I_A = 20.8$; $I_B = 79.0$; $I_C = 94.4\times10^{-40}$ gm. cm.^{2}

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ratios are collected in Table III. The contribution made by the torsional modes has been factorized out of the theoretical value for the a'' modes (9).

It may be seen from Tables I and II that the interpretation of several weak features required combination with the unobserved torsional mode. Further, in the infrared spectrum of solid CH_3CDO very weak features at 770 and 2117 cm.$^{-1}$, and in the vapor at 1192 cm.$^{-1}$, remain unexplained.

Solid Spectra

Most bands are at different positions in the solid and vapor spectra, some being at higher wave numbers in the solid and others at lower wave numbers. These changes provide an indication of the mechanism of intermolecular interaction between acetaldehyde molecules. The most significant are the changes undergone by the bands arising from the stretching modes of the carbonyl group and the aldehyde C—H and C—D groups. ν(C—H) and ν(C—D) are at higher wave numbers in the solid spectra indicating that hydrogen bonding between the C—H or C—D and the C=O groups is not involved in the interaction. It appears that the interaction is similar to that occurring in formaldehyde (11) and that similar arguments may be invoked to explain the changes in ν(C—H), ν(C—D), and the other vibrational modes with phase change, complicated, however, by the fact that interaction between vibrational modes is present in CH_3CDO.

There is also a difficulty in assigning the strong band at 1040 cm.$^{-1}$ in solid CH_3CDO. Its considerable intensity suggests that it might be a fundamental. However this would lead into a very much more complicated interpretation of the Raman bands and the vapor spectrum than that already given.

TABLE IV

ASSIGNMENT OF RAMAN SPECTRA OF $CH_3—\overset{\overset{O}{\|}}{C}—X$

	X = H	D	F	Cl	Br	I
a'	νCH_3 2964	2965		2994 p	2991	(3001)
	νCH_3 2917	2917	2940	2938 p	2929	2924
	2843	2097				
	νC—X 2751		815	594 p	555 p	540
	2731	2069				
	νC=O 1714	1702	1840	1802 p	1812 p	1793
	δCH_3 1426	1426	1428	1422 0.9	1418 0.85	1418
	δC—X 1391	1111	434 or 590	352 p or 438 p	304 p or 338 p	261 or 285
	δCH_3 1342	1343	1376	1361 p	1352 0.96	1350
	δCH_3 911	858	(1004)	957 p	(938) d?	(904)
	νCC 1109	1080	1106	1100 p	1084 p	1067
	δCCO 512	505	590 or 434	438 p or 352 p	338 or 304	285 or 261
a''	νCH_3 3001	2998	3038	3018 d	3015	
	δCH_3 1426	1426	1428	1422 0.9	1418 0.85	1418
	δCH_3 885	~825		(1032) p?	(988)	(943)
	δCX 767	674	(208)	(260) p?		

Brackets indicate tentative assignments.
Bands definitely polarized or depolarized are marked p *and* d *respectively.*
Numerical values of depolarization ratios are given for some bands where ambiguities might arise, and also question marks.

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Vibrational Assignment for Molecules $CH_3C\begin{matrix}O\\ \diagdown\\ X\end{matrix}$

The vibrational assignment for CH_3CHO and CH_3CDO is of great assistance in understanding the spectra of the acid halides for which X is F, Cl, Br, and I. In the case of acetyl chloride the Raman spectrum with depolarization ratios was obtained with the photoelectric instrument previously mentioned. For the fluoride (12), bromide (12), and iodide (7), however, the data were taken from the literature and were in all cases Raman data only. Our results for acetyl chloride are in good agreement with those of Reference 12 with the exceptions that the band at 260 cm.$^{-1}$ is not reported in Reference 12 and that the band at 957 cm.$^{-1}$ was found here to be polarized. In Table IV the spectra of these molecules in the liquid phase are assigned, where possible, according to the schematic representation given in column 1.

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HYDROLYSIS AND HYDRAZINOLYSIS OF ESTERS OF N,N-DIMETHYLDITHIOCARBAMIC ACID

A METHOD FOR THE PREPARATION OF MERCAPTANS[1]

By Marshall Kulka

ABSTRACT

A method has been developed for the preparation of mercaptans from alkyl and aralkyl chlorides. This consists of the condensation of sodium N,N-dimethyldithiocarbamate with halides followed by alkaline hydrolysis or hydrazinolysis of the resulting N,N-dimethyldithiocarbamates (IV). In the hydrazinolysis of IV, an insoluble solid by-product was formed which was identified as 3-hydrazino-4-amino-5-mercapto-4,1,2-triazole. Although this method was found to have wide scope a few failures were encountered. Nitro-derivatives of IV were sensitive to alkali or hydrazine and yielded only tars on attempted degradation. β-Phenoxyethyl N,N-dimethyldithiocarbamates (IX) were found to possess a labile alkyl–oxygen bond so that in the presence of alkali or hydrazine only the corresponding phenols were formed. The labile nature of the alkyl–oxygen bond ceased abruptly when the alkyl chain of IX was increased so that 3-*p*-chlorophenoxypropyl and 4-*p*-chlorophenoxybutyl mercaptans could be prepared in high yields.

In connection with our search for new insecticides a variety of mercaptans were required as intermediates. Of the most useful methods for the preparation of mercaptans even the thiourea method (21) is limited in scope. While thiourea reacts readily with alkyl and aralkyl bromides to form the isothiuronium salts, the reaction with many chlorides is extremely slow or does not proceed at all. Furthermore no nitrobenzyl mercaptans can be prepared by this method. The purpose of this investigation was to find a method for the preparation of mercaptans which would supplement the thiourea method.

v. Braun (5) observed that some aralkyl dithiocarbamates (I), which could be easily obtained from the corresponding aralkyl chlorides, when heated alone or with alkali gave the corresponding mercaptans (II) in high yields. One objection to the use of dithiocarbamates (I) as a source of mercaptans is the

$$\underset{\text{I}}{RS_2CNH_2} \longrightarrow \underset{\text{II}}{RSH} + HSCN$$

fact that they (I) are not stable enough to be purified by distillation. The esters of N,N-dimethyldithiocarbamic acid on the other hand may be distilled without decomposition and therefore they were adopted for degradation studies.

It was found that sodium N,N-dimethyldithiocarbamate (III), which is readily obtained from carbon disulphide, dimethylamine, and sodium hydroxide, reacts easily with chlorides including *p*-nitrobenzyl chloride, aryloxyalkyl chlorides, and *p*-nitrochlorobenzene, compounds which do not react with thiourea under normal conditions. The resulting N,N-dimethyldithiocarbamates (IV) which were obtained in high yields (Table I) were not only

[1]*Manuscript received April 4, 1956.*
Contribution from the Dominion Rubber Company Limited Research Laboratories, Guelph, Ontario.

thermally stable but also exhibited considerable resistance to hydrolysis. Prolonged heating with aqueous acids or in acetic hydrochloric acid solution did not produce any appreciable change while heating with aqueous alkali caused only partial hydrolysis. However when IV was heated under reflux for five hours or longer with five moles of aqueous-alcoholic alkali, the mercaptide (V) was formed in high yield together with sodium sulphide, sodium carbonate, water, and dimethylamine. A variety of mercaptans were successfully prepared (Table II) from the corresponding chlorides by this two stage

$$\underset{\text{III}}{RCl} + NaS_2CN(CH_3)_2 \longrightarrow \underset{\text{IV}}{RS_2CN(CH_3)_2} + NaCl$$

$$\underset{\text{IV}}{RS_2CN(CH_3)_2} + 5NaOH \longrightarrow \underset{\text{V}}{RSNa} + Na_2S + Na_2CO_3 + 2H_2O + NH(CH_3)_2$$

method and a few failures were encountered. *p*-Nitrobenzyl N,N-dimethyldithiocarbamate (IV, R = *p*-$NO_2C_6H_4CH_2$) like *p*-nitrobenzyl isothiuronium chloride is sensitive to alkali and attempted hydrolysis yielded only tar. Also *p*-xylylene bis-N,N-dimethyldithiocarbamate, *p*-$(CH_3)_2NCS_2CH_2C_6H_4CH_2S_2CN(CH_3)_2$, remained unchanged after prolonged heating with excess alkali.

Another method of degradation of IV, namely hydrazinolysis, was investigated. When benzyl N,N-dimethyldithiocarbamate (IV, R = $C_6H_5CH_2$) was heated under reflux with excess hydrazine hydrate in ethanol, an 82% yield of benzyl mercaptan (II, R = $C_6H_5CH_2$) was obtained. In addition a highly insoluble white compound precipitated from the reaction mixture and proved to be 3-hydrazino-4-amino-5-mercapto-4,1,2-triazole (VIII). This (VIII) must

$$\underset{\text{IV}}{RS_2CN(CH_3)_2} + H_2NNH_2 \longrightarrow \underset{\text{II}}{RSH} + \underset{\text{VI}}{H_2NNHCSN(CH_3)_2}$$

$$\underset{\text{VI}}{H_2NNHCSN(CH_3)_2} + H_2NNH_2 \longrightarrow \underset{\text{VII}}{H_2NNHCSNHNH_2} + NH(CH_3)_2$$

$$2\ \text{VII} \longrightarrow \underset{\text{VIII}}{\text{(3-hydrazino-4-amino-5-mercapto-4,1,2-triazole)}} + H_2NNH_2 + H_2S$$

be formed from the thiosemicarbazide (VI) which with hydrazine could produce thiocarbohydrazide (VII) and dimethylamine. Two moles of VII or alternatively one mole of VI and one mole of VII could undergo cyclization to form VIII. That this is the mechanism for the formation of VIII is indicated by the fact that authentic samples of diethyl xanthate or thiocarbohydrazide (19, 20) when heated with hydrazine in ethanol formed VIII.

It is noteworthy that where alkaline hydrolysis failed, hydrazinolysis succeeded in the case of *p*-xylylene bis-N,N-dimethyldithiocarbamate. *p*-Xylylene dimercaptan was obtained in 77% yield after prolonged treatment with hydrazine. However, attempted hydrazinolysis of *p*-nitrobenzyl and *p*-nitrophenyl

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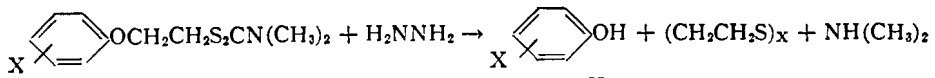
N,N-dimethyldithiocarbamates like attempted alkaline hydrolysis yielded only resinous materials.

In view of the known anomalous reactions of some phenoxyalkyl halides it was necessary to investigate the conversion of these halides to the phenoxyalkyl mercaptans. Gordon (10) and Lyle, Dewitt, and Pattison (16) observed that 2-phenoxyethyl halides did not produce the Grignard reagents in the presence of magnesium and ether. Instead the alkyl–oxygen bond was severed and phenol was formed. On the other hand phenoxyalkyl halides with alkyl chain greater than three carbon atoms behaved normally in respect to Grignard formation (16). Also, abnormal results were obtained in the reaction of 2-phenoxyethyl bromide with sodium cyanide but not in the case of 3-phenoxypropyl bromide which yielded γ-phenoxybutyronitrile (10). Crane and Rydon (6) have found that compounds of the type $C_6H_5OCH_2CH_2\overset{+}{S}R_2$, but not of type $C_6H_5OCH_2CH_2SR$, are split by dilute alkali to give initially $R_2\overset{+}{S}CH{=}CH_2$ and sodium phenoxide.

In this investigation all phenoxyalkyl halides reacted normally with III to give the corresponding phenoxyalkyl dimethyldithiocarbamates (Table I). However when the latter were subjected to alkaline hydrolysis or hydrazinolysis it was soon found that 2-phenoxyethyl N,N-dimethyldithiocarbamates (IX) gave no mercaptans. Instead the alkyl–oxygen bond of IX was severed and the corresponding phenol (X) was obtained in high yield. The



IX X

same results were obtained when β-*p*-*t*-butylphenoxyethyl bromide was treated with thiourea and the resulting isothiuronium salt heated with aqueous alkali. The sulphur–alkyl bond in the compound obtained by substituting sulphur for the oxygen atom in IX is also labile in nature. Thus the reaction of β-*p*-chlorophenylmercaptoethyl N,N-dimethyldithiocarbamate with hydrazine in ethanol gave *p*-chlorothiophenol in 50% yield.

It was expected that steric hindrance might play a part in retarding the cleavage of the alkyl–oxygen bond in IX. Therefore β-(2,4-dichlorophenoxy) ethyl and β-(2-*t*-butyl-4-methylphenoxy)ethyl N,N-dimethyldithiocarbamates were prepared and then subjected to hydrazinolysis. The products of the reactions were 2,4-dichlorophenol and 2-*t*-butyl-4-methylphenol respectively showing that the ortho bulky groups do not strengthen the alkyl–oxygen bond.

The weak nature of the alkyl–oxygen bond of IX ends abruptly when the length of the alkyl chain is increased. Thus 3-*p*-chlorophenoxypropyl and 4-*p*-chlorophenoxybutyl mercaptans were prepared in 85 and 87% yields by the hydrazinolysis of the corresponding phenoxyalkyl N,N-dimethyldithiocarbamates. There is also a difference in the light stability of IX and its higher homologues. The phenoxypropyl and phenoxybutyl N,N-dimethyldithiocarbamates remain unchanged on standing while IX turns pink or red very quickly on exposure to light.

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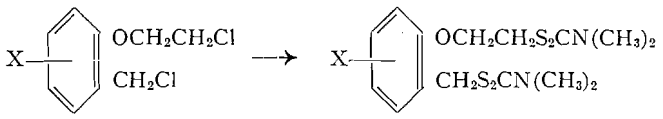
It has been already reported (14) that when *o*-(2-chloroethoxy)benzyl chlorides (XI) are treated with thiourea and the resulting *o*-(2-chloroethoxy) benzylisothiuronium chlorides subjected to alkaline cleavage, no mer-



XI XII

captans are formed because simultaneous cyclization occurs to give the seven-membered ring compounds the 2,3-dihydrobenzo(*f*)-1,4-oxathiepins. With sodium dimethyldithiocarbamate (III), 2-(2-chloroethoxy)-4-methylbenzyl chloride (XI, X = 4-CH_3) yielded the bis-dithiocarbamate (XII) but alkaline cleavage of this did not yield a dimercaptan nor 7-methyl-2,3-dihydrobenzo(*f*)-1,4-oxathiepin. Instead a complex mixture was formed whose components were not identified.

EXPERIMENTAL

Sodium N,N-Dimethyldithiocarbamate

To stirred 40% dimethylamine (340 ml.) was added dropwise first carbon disulphide (185 ml.) and then sodium hydroxide (120 gm.) in water (300 ml.), the reaction temperature being kept at 10–15° by cooling. The reaction mixture was stirred at room temperature for two hours and then concentrated *in vacuo* to about half the original volume and allowed to cool. The precipitate was filtered, washed with a little cold acetone, and air-dried. The yield from three successive crops was 361 gm. This product, which is a hydrate melting at 106–108°, was pure enough to be used in the preparation of the N,N-dimethyldithiocarbamic esters.

Preparation of the N,N-Dimethyldithiocarbamates (Table I)

To a solution of sodium N,N-dimethyldithiocarbamate (0.3 mole) in acetone (400 ml.) was added the halide (0.25 mole), and the reaction mixture was heated under reflux for periods depending upon the reactivity of the halide. With alkyl bromides and benzyl chlorides the reaction was exothermic and required little heating. Three hours' refluxing time was required in the case of the phenoxyalkyl chlorides, and in the extreme case of *p*-nitrochlorobenzene several days were required. The precipitated sodium halide was filtered, the acetone was distilled off from the filtrate, and the residue was either distilled or crystallized from methanol.

Hydrolysis of N,N-Dimethyldithiocarbamates to Mercaptans (Table II)

This is exemplified by the hydrolysis of benzyl N,N-dimethyldithiocarbamate to benzyl mercaptan. To a solution of sodium hydroxide (15 gm.) in water (30 ml.) was added benzyl N,N-dimethyldithiocarbamate (7) (15 gm.) and ethanol (150 ml.), and the reaction mixture was heated under reflux for five hours. Dimethylamine was given off through the condenser and could be caught in a dry ice trap, and sodium carbonate precipitated from the reaction mixture. The ethanol was removed and the residue acidified. Carbon dioxide and hydrogen sulphide were liberated. The precipitated mercaptan was ex-

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TABLE I

THE PREPARATION OF N,N-DIMETHYLDITHIOCARBAMATES $RS_2CN(CH_3)_2$ FROM THE CORRESPONDING HALIDES, RX

$RS_2CN(CH_3)_2$ R =	Halide used X =	Reaction time	M.p., °C.	% Yield	Empirical formula	Analyses			
						Calc.		Found	
						C	H	C	H
$C_6H_5CH_2$ (7)	Cl	15 min.	40–41	82					
p-$ClC_6H_4CH_2$	Cl	15 min.	54–55	82	$C_{10}H_{12}NClS_2$	48.88	4.89	48.96	4.79
2,4-$DiClC_6H_3CH_2$	Cl	15 min.	82–83	94	$C_{10}H_{11}NCl_2S_2$	42.86	3.93	43.32	3.94
3,4-$DiClC_6H_3CH_2$	Cl	15 min.	75–76	95	$C_{10}H_{11}NCl_2S_2$	42.86	3.93	43.11	4.04
2,4-$DiCH_3C_6H_3CH_2$	Cl (13)	15 min.	B.p. 219–222 (10 mm.)	80	$C_{12}H_{17}NS_2$	60.25	7.11	60.26	7.05
p-$NO_2C_6H_4CH_2$	Cl	15 min.	106–107	95	$C_{10}H_{12}O_2N_2S_2$	46.88	4.69	47.20	4.48
3-NO_2-4-$CH_3OC_6H_3CH_2$	Cl	15 min.	102–103	82	$C_{11}H_{14}N_2O_3S_2$	46.15	4.90	46.07	4.91
p-$NO_2C_6H_4$	Cl	10 days	156–157	20	$C_9H_{10}N_2O_2S_2$	44.63	4.13	45.16	4.10
2,4-$DiNO_2C_6H_4$	Cl	15 min.	152–153	84	$C_9H_9N_3O_4S_2$	37.62	3.14	37.70	3.00
$C_6H_5CH_2CH_2$	Cl	3 hr.	45–46	92	$C_{11}H_{15}NS_2$	58.66	6.67	58.85	6.53
$CH_3(CH_2)_{10}CH_2$	Br	30 min.	39–40	76	$C_{15}H_{31}NS_2$	62.28	10.73	62.11	10.66
$CH_3(CH_2)_{14}CH_2$	Br	30 min.	48–49	78	$C_{19}H_{39}NS_2$	66.09	11.31	66.06	11.14
$CH_3(CH_2)_4CH_2$	Br	30 min.	B.p. 167–168 (10 mm.)	86	$C_9H_{19}NS_2$	52.69	9.27	52.96	9.48
p-$(CH_3)_3CC_6H_4OCH_2CH_2$	Cl	4 hr.	61–62	90	$C_{15}H_{23}NOS_2$	60.61	7.74	60.80	7.60
p-$CH_3C_6H_4OCH_2CH_2$	Cl	3 hr.	64–65	88	$C_{12}H_{17}NOS_2$	56.47	6.66	56.55	6.58
p-$ClC_6H_4OCH_2CH_2$	Cl	3 hr.	73–74	90	$C_{11}H_{14}NOClS_2$	47.91	5.08	47.88	4.96
2,4-$DiClC_6H_3OCH_2CH_2$	Cl	3 hr.	73–74	98	$C_{11}H_{13}NOCl_2S_2$	42.58	4.19	42.40	4.26
2-$(CH_3)_3C$-4-$CH_3C_6H_3OCH_2CH_2$	Cl (14)	3 hr.	78–79	96	$C_{16}H_{25}NOS_2$	61.73	8.04	61.83	7.94
p-$ClC_6H_4O(CH_2)_3$	Br (9)	1 hr.	92–93	82	$C_{12}H_{16}NOClS_2$	49.74	5.53	50.06	5.25
p-$ClC_6H_4O(CH_2)_4$	Cl	3 hr.	64–65	85	$C_{13}H_{18}NOClS_2$	51.40	5.93	51.58	5.71
p-$[(CH_3)_2NCS_2CH_2]_2C_6H_4$	Cl	15 min.	178–179	96	$C_{14}H_{20}N_2S_4$	48.84	5.81	48.96	5.79
$[(CH_3)_2NCS_2CH_2CH_2]_2S$	Cl	15 min.	111–112	80	$C_{10}H_{20}N_2S_5$	36.59	6.10	36.87	6.01
2-$[(CH_3)_2NCS_2CH_2]$-4-$CH_3C_6H_3OCH_2CH_2S_2CN(CH_3)_2$	Cl (14)	3 hr.	114–115	87	$C_{16}H_{24}N_2OS_4$	49.48	6.18	49.64	6.07
p-$ClC_6H_4CH_2SCH_2CH_2$	Cl*	1 hr.	50–51	90	$C_{12}H_{16}NClS_3$	47.14	5.22	47.38	5.14
p-$ClC_6H_4SCH_2CH_2$	Br*	15 min.	96–97	98	$C_{11}H_{11}NClS_3$	45.29	4.80	45.26	4.71

**These were prepared from p-chlorobenzyl mercaptan and ethylene dichloride and from p-chlorothiophenol and ethylene dibromide respectively by the method of Patterson and du Vigneaud (18).*

tracted with benzene, the extract washed with water, and the solvent removed. The residue distilled at 77–79° at 12 mm. pressure yielding a colorless odiferous liquid (7.2 gm. or 86%) of *benzyl mercaptan.*

Hydrazinolysis of N,N-Dimethyldithiocarbamates to Mercaptans (Table II)

This is exemplified by the hydrazinolysis of 3-*p*-chlorophenoxypropyl N,N-dimethyldithiocarbamate to *3-p-chlorophenoxypropyl mercaptan.* A solution of 3-*p*-chlorophenoxypropyl N,N-dimethyldithiocarbamate (12 gm.), 85% hydrazine hydrate (20 ml.), and ethanol (80 ml.) was heated under reflux for 30 hr. Dimethylamine was given off through the condenser and a white solid precipitated from the reaction mixture. The white solid (1.1 gm.) was filtered, washed with methanol, water, methanol, and hot benzene, and dried. It melted at 233–235° with decomposition and did not depress the melting point of 3-hydrazino-4-amino-5-mercapto-4,1,2-triazole (20). The filtrate was taken to dryness *in vacuo.* The residue was treated with water and extracted with benzene. The extract was washed with water and the solvent removed. The residue distilled at 153–155° at 10 mm. pressure as a colorless liquid with odor not too objectionable. The yield was 7.2 gm. or 85%, $n_D^{24} = 1.5620$. Anal. calc. for $C_9H_{11}OClS$: C, 53.33; H, 5.43. Found: C, 53.37, 53.37; H, 5.41, 5.14.

TABLE II

THE PREPARATION OF MERCAPTANS, RSH, FROM THE CORRESPONDING N,N-DIMETHYLDITHIOCARBAMATES, $RS_2CN(CH_3)_2$, BY HYDROLYSIS (METHOD A) AND BY HYDRAZINOLYSIS (METHOD B)

Mercaptan, R =	Method of prep.	B.p.	n_D^{20}	% Yield
$C_6H_5CH_2$ (8)	A		1.5730	86
	B	73 (10 mm.)		82
p-$ClC_6H_4CH_2$ (15)	A	105 (10 mm.)		95
2,4-$DiClC_6H_3CH_2$ (4)	A	123–125 (10 mm.)	1.6000	88
3,4-$DiClC_6H_3CH_2$ (15, 4)	A	132–134 (11 mm.)	1.6015	93
2,4-$Di(CH_3)C_6H_3CH_2$) (13)	A[a]	100–102 (10 mm.)	1.5610	70
$C_6H_5CH_2CH_2$ (5, 12)	A	95– 98 (12 mm.)		66
$CH_3(CH_2)_4CH_2$ (2)	A*	155–160		61
$CH_3(CH_2)_{10}CH_2$ (21)	A*	134–135 (10 mm.)	1.4575	86
$CH_3(CH_2)_{14}CH_2$	A*	182–188 (10 mm.)		65
p-$ClC_6H_4O(CH_2)_3$	B[b]	153–155 (10 mm.)	1.5620	85
p-$ClC_6H_4O(CH_2)_4$	B[c]	170–172 (10 mm.)	1.5550	87
p-$SHCH_2C_6H_4CH_2SH$ (1)	B†	M.p. 44–45		77

**The reaction time required was 24 hr. instead of 5.*

†*The reaction time required was three days instead of 30 hr. This compound was also prepared in 86% yield by the thiourea method.*

ANALYSES

[a]*Calc. for $C_9H_{12}S$: C, 71.05; H, 7.89. Found: C, 71.01; H, 7.78.*

[b]*Calc. for $C_9H_{11}OClS$: C, 53.33; H, 5.43. Found: C, 53.37; H, 5.41.*

[c]*Calc. for $C_{10}H_{13}OClS$: C, 55.43; H, 6.00. Found: C, 55.41; H, 5.85.*

Preparation of Sulphides

This is exemplified by the preparation of *3-p-chlorophenoxypropyl p-chlorobenzyl sulphide.*

To a solution of potassium hydroxide (0.7 gm.) in methanol (40 ml.) was added *p*-chlorobenzyl chloride (2.0 gm.) and 3-*p*-chlorophenoxypropyl mercaptan (2.3 gm.), and the resulting solution was heated under reflux for 10 min. The precipitated potassium chloride was filtered, the methanol removed from the filtrate, and the residue distilled. The colorless liquid (3.2 gm.)

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which boiled at 257° at 10 mm. pressure solidified on cooling. The cake was pulverized, washed with methanol, and dried. The white product melted at 37–38° alone or in admixture with the compound prepared from *p*-chlorobenzyl mercaptan and 3-*p*-chlorophenoxypropyl bromide. Anal. calc. for $C_{16}H_{16}OCl_2S$: C, 58.72; H, 4.89. Found: C, 58.72, 58.78; H, 4.64, 4.95.

The above method was also used for the preparation of the following sulphides:

Bis-p-chlorobenzyl sulphide from *p*-chlorobenzyl mercaptan and *p*-chlorobenzyl chloride in 80% yield. It melted at 42–43°; literature (17) 41°.

Benzyl 3-nitro-4-methoxybenzyl sulphide from benzyl mercaptan and 3-nitro-4-methoxybenzyl chloride in 78% yield, m.p. 55–56°. Anal. calc. for $C_{15}H_{15}NO_3S$: C, 62.30; H, 5.19. Found: C, 62.30; H, 5.20.

p-Chlorobenzyl β-p-t-butylphenoxyethyl sulphide from *p*-chlorobenzyl mercaptan and *β-p-t*-butylphenoxyethyl bromide in 90% yield, b.p. 250° (10 mm.). Anal. calc. for $C_{19}H_{23}OClS$: C, 68.17; H, 6.88. Found: C, 68.07; H, 6.86.

p-Chlorobenzyl n-dodecyl sulphide from *n*-dodecyl mercaptan and *p*-chlorobenzyl chloride in 80% yield, b.p. 235–236° (10 mm.), $n_D^{20} = 1.5155$. Anal. calc. for $C_{19}H_{31}ClS$: C, 69.82; H, 9.50. Found: C, 69.89; H, 9.35.

Hydrazinolysis of β-2,4-Dichlorophenoxyethyl N,N-Dimethyldithiocarbamate to 2,4-Dichlorophenol

A reaction mixture of β-2,4-dichlorophenoxyethyl N,N-dimethyldithiocarbamate (20 gm.), 85% hydrazine hydrate (20 ml.), and ethanol (100 ml.) was heated under reflux for 30 hr. The white precipitate was filtered from the cooled reaction mixture and the filtrate taken to dryness *in vacuo*. The residue was treated with water and extracted with benzene. The benzene extract was washed with water and the solvent removed. The residue distilled at 89–93° at 10 mm. pressure and the distillate (9 gm. or 86%) which solidified melted at 38–40° alone or in admixture with 2,4-dichlorophenol. The white precipitate was extracted with boiling benzene leaving a benzene-insoluble product (1.5 gm.) which melted at 233–235° with decomposition and did not depress the melting point of 3-hydrazino-4-amino-5-mercapto-4,1,2-triazole (20). The benzene extract was concentrated and cooled. A white amorphous malodorous substance (0.4 gm., m.p. 80–90°) precipitated which gave analyses agreeing with those of ethylene sulphide polymer.

In the same way *β-p-chlorophenoxyethyl*, *β-p-t-butylphenoxyethyl*, *β-p-tolyloxyethyl*, and *β-(2-t-butyl-4-methylphenoxy)ethyl N,N-dimethyldithiocarbamates* hydrazinolyzed to *p-chlorophenol*, *p-t-butylphenol*, *p-cresol*, and *2-t-butyl-4-methylphenol* respectively.

Alkaline Cleavage of β-p-t-Butylphenoxyethyl Bromide and N,N-Dimethyldithiocarbamate

A solution of *β-p-t*-butylphenoxyethyl bromide (55 gm.), thiourea (20 gm.), and ethanol (200 ml.) was heated under reflux for 24 hr. To this was added sodium hydroxide (20 gm.) in water (100 ml.) and the resulting reaction mixture was heated under reflux for 5 hr. The cooled reaction mixture was diluted with water, acidified, and extracted with benzene. The benzene extract was washed with water, the solvent removed, and the residue distilled. There

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was obtained an alkali-soluble distillate (22 gm.), b.p. 120–125° (11 mm.), which when crystallized from benzene melted at 98–100° either alone or in admixture with *p-t*-butylphenol. This phenol was also obtained when *β-p-t*-butylphenoxyethyl N,N-dimethyldithiocarbamate was heated with alcoholic alkali as above.

3-Hydrazino-4-amino-5-mercapto-4,1,2-triazole

A reaction mixture of thiocarbohydrazide (2 gm.) (11), ethanol (10 ml.), and 85% hydrazine hydrate (5 ml.) was heated under reflux for 24 hr. The white precipitate was filtered, washed with methanol, water, methanol, and hot benzene in that order. The white powder (0.85 gm.) melted at 233–235° with decomposition. Stollé and Bowles (20) give a melting–decomposition point of 228°. A similar prolonged treatment of diethyl xanthate also gave 3-hydrazino-4-amino-5-mercapto-4,1,2-triazole.

4-p-Chlorophenoxybutyl Chloride

A reaction mixture of *p*-chlorophenol (65 gm.), 1,4-dichlorobutane (100 ml.), a solution of potassium hydroxide (30 gm.) in water (100 ml.), and benzene (200 ml.) was heated under reflux for three days. The organic layer was separated, washed with aqueous alkali and with water, and the solvent and excess 1,4-dichlorobutane were removed *in vacuo*. The residue distilled at 159–162° (10 mm.) as a colorless liquid, $n_D^{22} = 1.5340$, yield 45 gm. Anal. calc. for $C_{10}H_{12}OCl_2$: C, 54.80; H, 5.48. Found: C, 54.35, 54.71; H, 5.26, 5.39.

The residue from the distillation when crystallized from benzene–methanol yielded 21 gm. of white prisms of *1,4-bis-p-chlorophenoxybutane*, m.p. 107–108°. Anal. calc. for $C_{16}H_{16}O_2Cl_2$: C, 61.64; H, 5.14. Found: C, 61.74; H, 5.12.

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THE APPLICATION OF INTERPOLATION THEORY TO DATA ON THE ADSORPTION OF NITROGEN, OXYGEN, AND ARGON ON RUTILE[1]

By J. M. Honig and L. H. Reyerson[2]

ABSTRACT

The interpolation theory has been applied to data on the adsorption of nitrogen, oxygen, and argon on rutile at 77° K. It has been demonstrated that the oxygen and argon data cannot be interpreted on the basis of the Langmuir model, modified by the introduction of surface heterogeneity effects. The interpolation theory verifies, however, that the distribution of adsorption energies among surface sites, obtained by inversion of the nitrogen isotherm, is physically significant, and that nitrogen is suitable for BET surface area calculations.

INTRODUCTION

The inadequacy of the Langmuir model in the interpretation of gas adsorption phenomena is well known. Nevertheless, a variant of this model, the BET multilayer adsorption theory, has found widespread use in the estimation of surface areas, though it is recognized that the results cannot be completely reliable. Attempts have been made to improve on the Langmuir model by taking account of the energy heterogeneity of the surface (2, 3, 10, 11, 12, 13, 17, 20, 21, 22, 23). While this is a step in the right direction, the results are still unsatisfactory because lateral interactions are left out of consideration. On the other hand, a reasonably rigorous treatment of both effects (12) or even a rather specialized approach along these lines (1, 8, 9) leads to complicated equations. In practice one is therefore often forced to return to the use of the BET equation in the analysis of gas adsorption isotherms.

In order to have confidence in the results of such a simple approach, one must determine how well the data conform to the restrictive assumptions of the Langmuir or BET model. Thermodynamic considerations (see for example (4, 5, 16)) have been quite helpful for this purpose. Recently a new approach has been cited in the literature (14, 15) in which it was shown that all data conforming to the Langmuir model, the BET model, or to a theory dealing with surface heterogeneity effects must lie within well-defined limits on a plot of surface coverage versus pressure. Details for the construction of these limits by use of the so-called interpolation theory (18) have been provided. Such an analysis should aid in deciding whether the simple adsorption theories are applicable to a given adsorbate–adsorbent system. For, if a given set of datum points is found to fall outside the interpolation limits, then the Langmuir model and the various modifications which include surface heterogeneity effects are hopelessly inadequate. In such cases it is obviously not justifiable to use the

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[2]*One of us (LHR) gratefully acknowledges funds received from the graduate school in partial support of this work. Both authors are indebted to Mr. Chi Chang for performing the calculations on which Figs. 1, 2, and 3 are based.*

isotherm data to compute a distribution of adsorption energies among surface sites, and even the BET method of determining at what point on the isotherms monolayer coverage is complete is open to criticism.

The purpose of the present article is to provide examples showing how the interpolation procedure operates. The method will be utilized to settle a problem raised by Honig and Reyerson (13) in connection with a study on the adsorption of nitrogen, oxygen, and argon on rutile.

THE INTERPOLATION THEORY

Any adsorbent–adsorbate system which conforms to the modified Langmuir theory is characterized by an adsorption isotherm of the form (11):

$$[1] \qquad \frac{n}{n_m} \equiv \theta(p, T) = \int_{\epsilon_0}^{\epsilon_m} \frac{dF(\epsilon)}{1+(\beta(\epsilon, T)/p)e^{-\epsilon/kT}}$$

where n and n_m are the number of adsorbate molecules held on the surface at a pressure p and at monolayer coverage respectively, θ is the fraction of the surface covered at pressure p and temperature T, $dF(\epsilon) \equiv f(\epsilon)d\epsilon$ is the fraction of sites associated with adsorption energies in the range ϵ to $\epsilon+d\epsilon$, ϵ_0 and ϵ_m are respectively the minimum and maximum values of ϵ encountered on the surface, and β is a quantity defined by:

$$[2] \qquad \beta(\epsilon, T) = (2\pi mkT/h^2)^{3/2}kT\, j_0(T)/j_s(\epsilon, T)$$

where m is the mass of the adsorbate particles, while j_g and j_s represent the partition functions of the particles in the gas and in the adsorbed phases respectively. Note that the latter quantity depends on ϵ (7, 11, 12).

Eq. [1] represents a one-to-one correspondence between θ and F. Rosenbloom (18) has developed a theory in which he proves that one can select two distribution functions $F_a(\epsilon)$ and $F_b(\epsilon)$ such that the corresponding equations $\theta_a(p, T)$ and $\theta_b(p, T)$ form the limits, mentioned in the introduction, within which the data must fall if eq. [1] is to apply. For details of the construction of the extremal isotherms the reader is referred to the original publication (14).

In what follows it suffices to note that the bounding isotherms θ_a and θ_b are adjusted to a given set of experimental data by the arbitrary selection of a set of reference points through which the functions θ_a and θ_b are required to pass. One then observes whether the remaining experimental points lie within the region which is bounded by the functions θ_a and θ_b. This gives an indication as to the applicability of the Langmuir model or of models combining the Langmuir postulates with the concept of surface heterogeneity. For, it is evident from the remarks that if any points fall outside this region, this is a clear indication that eq. [1] cannot be used in the interpretation of the data.

The calculations cited below were based on the use of the following relations:

$$[3] \qquad \theta_a(p, T) = \frac{(\theta_2-\theta_1)p+[\theta_1p_2(1-\theta_2)-\theta_2p_1(1-\theta_1)]}{(\theta_2-\theta_1)p+[p_2(1-\theta_2)-p_1(1-\theta_1)]},$$

$$[4] \qquad \theta_b(p, T) = \frac{\theta_1\theta_2(p_1-p_2)}{p_1p_2(\theta_2-\theta_1)/p+(\theta_2p_1-\theta_1p_2)}.$$

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These equations require the selection of two reference points (θ_1, p_1) and (θ_2, p_2) from among the data. It was shown in (14) that [3] and [4] result upon simplification of the expression for the "third-order" limiting isotherms. Being approximate, they bound a wider region in the θ vs. p diagram than the exact functions, and thus less precise information is obtained. On the other hand, no unknown parameters are involved, and the calculations are relatively simple.

One should note that the quantity n_m cancels from both sides of [4] when θ is replaced by n/n_m. On the other hand, the value of n_m must be specified for use in [3]. It has been verified, however, that the dependence of θ_a on n_m is not marked. It has also been established that none of the conclusions reached below would be invalidated by the selection of n_m values which differ radically from the set adopted below.

APPLICATION TO NITROGEN, OXYGEN, ARGON ADSORPTION ISOTHERMS

The interpolation theory will now be applied to the adsorption on nitrogen, oxygen, and argon observed at 77° K. (13). The isotherms are drawn as dotted lines through the experimental points in Figs. 1, 2, and 3. Two sets of extremal isotherms are entered as heavy curves on each figure. The reference data used in the computation of each set are listed in the captions of the diagrams. The areas bounded by each set of extremals are shaded and are labelled A and B respectively. The low pressure region of Fig. 1 has been expanded in the inset

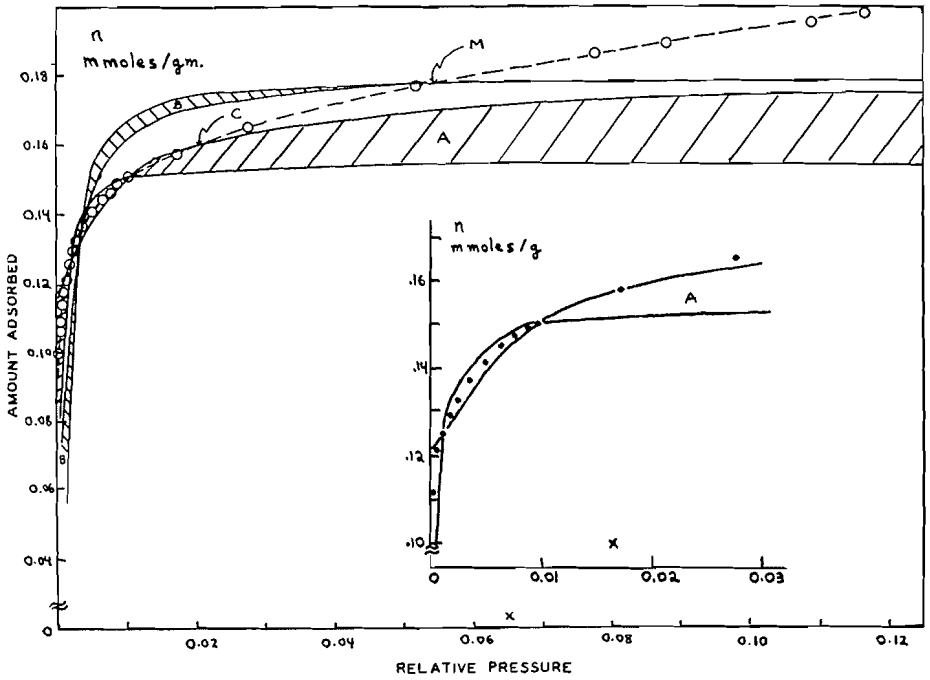

FIG. 1. Limiting isotherms for the adsorption of nitrogen on rutile at 77° K. Reference points for Area A: $n_1 = 0.125$ mmoles/gm.; $p_1 = 0.13$ cm. Hg; $n_2 = 0.149$ mmoles/gm.; $p_2 = 0.78$ cm. Hg. Reference points for Area B: $n_1 = 0.137$ mmoles/gm.; $p_1 = 0.29$ cm. Hg; $n_2 = 0.177$ mmoles/gm.; $p_2 = 4.12$ cm. Hg; $n_m = 0.179$ mmoles/gm. Open circles are experimental points, connected by dotted line; shaded regions are areas bounded by extremal isotherms.

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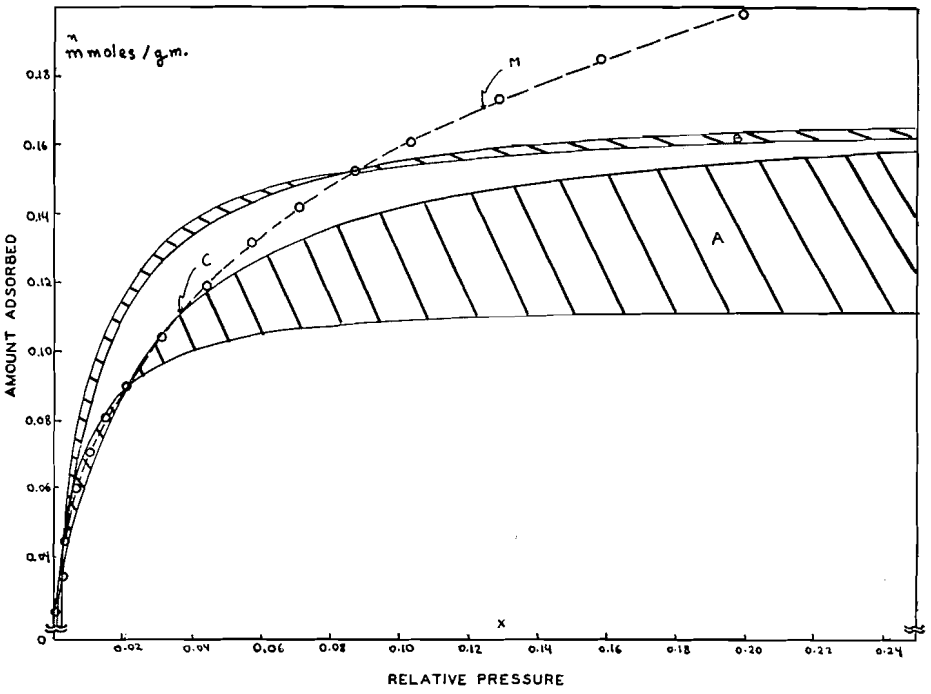

FIG. 2. Limiting isotherms for the adsorption of oxygen on rutile at 77° K. Reference points for Area A: $n_1 = 0.0346$ mmoles/gm.; $p_1 = 0.040$ cm. Hg; $n_2 = 0.0901$ mmoles/gm.; $p_2 = 0.34$ cm. Hg. Reference points for Area B: $n_1 = 0.0346$ mmoles/gm.; $p_1 = 0.040$ cm. Hg; $n_2 = 0.142$ mmoles/gm.; $p_2 = 1.13$ cm. Hg; $n_m = 0.171$ mmoles/gm. Open circles are experimental points, connected by dotted line; shaded regions are areas bounded by extremal isotherms.

to Fig. 1. The values of n_m were taken from Table II of (13). Attention is directed to the interlacing structure of θ_a and θ_b, which alternately form lower and upper bounds in the intervals marked off by the reference points p_1 and p_2.

Inspection of the graphs shows that the low pressure points fall within the bounds prescribed by the third-order theory. However, in every case there exists a point labelled C beyond which all experimental points fall outside the area A. These findings can be qualitatively related to the results of the BET theory which predicts the onset of multilayer formation beyond the point labelled M on each isotherm.[3] The formation of higher layers clearly violates the Langmuir postulate which excludes the case of multilayer adsorption. It is therefore necessary for the high pressure points to fall above the upper limit prescribed for the first layer by the interpolation theory.

Further examination indicates, however, that the isotherms cross the theoretical limits at a point C below the point M where monolayer coverage is essentially complete. Thus, for argon the point C occurs at $n = 0.10$ mmoles ($\theta = 0.62$), and for oxygen, at $n = 0.11$ mmoles ($\theta = 0.64$). On the other hand, the nitrogen isotherm remains within the limiting bounds up to $n = 0.16$ mmoles ($\theta = 0.90$).

[3]*The presence of multilayer condensation is clearly established by unpublished work of the authors in the partial pressure range* $0.1 \leqslant p/p_0 \leqslant 0.9$. *All three adsorbates yield type II isotherms in the BET classification.*

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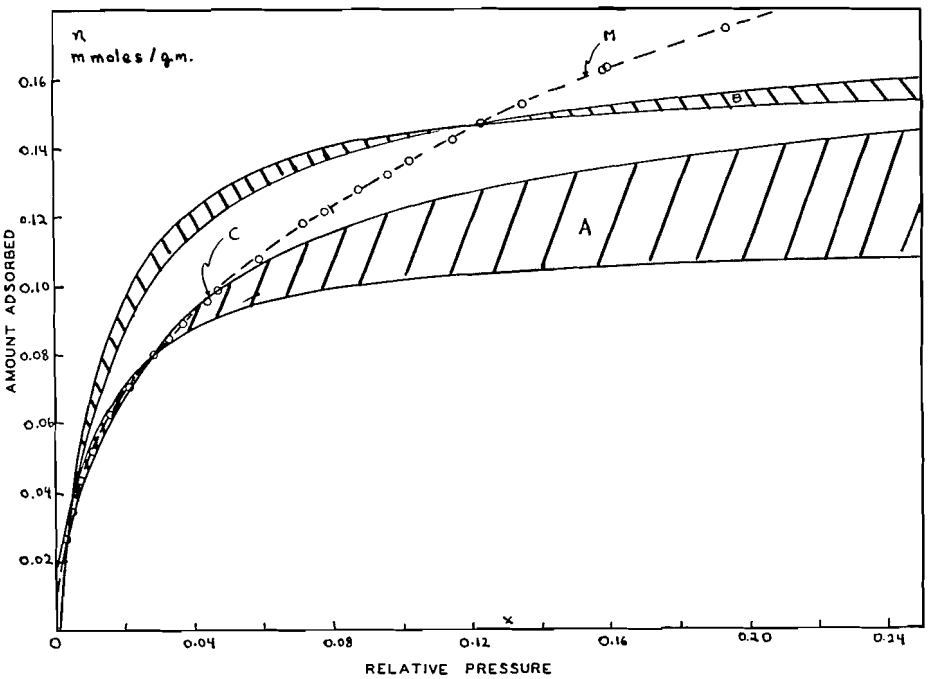

FIG. 3. Limiting isotherms for the adsorption of argon on rutile at 77° K. Reference points for Area A: $n_1 = 0.0264$ mmoles/gm.; $p_1 = 0.08$ cm. Hg; $n_2 = 0.0808$ mmoles/gm.; $p_2 = 0.69$ cm. Hg. Reference points for Area B: $n_1 = 0.0264$ mmoles/gm.; $p_1 = 0.08$ cm. Hg; $n_2 = 0.142$ mmoles/gm.; $p_2 = 2.32$ cm. Hg; $n_m = 0.164$ mmoles/gm. Open circles are experimental points, connected by dotted line; shaded regions are areas bounded by extremal isotherms.

These findings can be checked by the selection of other reference points. It has been verified that when these are chosen from the data below the point C, the isotherm is always found to cross the third-order limiting curve near point C. However, if one of the reference points is selected from the data falling above point C, the limiting curves bound an area B which does not coincide with the experimental points except near (θ_1, p_1) and (θ_2, p_2).

DISCUSSION OF RESULTS

The results indicate that all adsorption data remain within their extremal bounds at low surface coverage, provided that the reference points are selected, in conformity with the simplifying assumptions of the interpolation theory, from the region below point C.

However, while the nitrogen isotherm remains within its prescribed bounds until monolayer coverage is almost complete, the oxygen and argon isotherms deviate from their prescribed limits much sooner. Evidently the system nitrogen: rutile conforms more closely to the modified Langmuir model than the other two systems. This behavior can probably be explained on the basis of a statement by Drain (6). Nitrogen possesses a quadrupole moment of appreciable magnitude, which contributes to the physical binding of nitrogen molecules to the surface. In oxygen or argon this contribution is absent, and the binding energy to the surface is appreciably lower. As a result, factors such as lateral

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interactions and surface mobility, which are ignored in the Langmuir model, play a more significant role for oxygen or argon than for nitrogen.

Undoubtedly the experimental conditions are such that even for nitrogen the modified Langmuir model is a poor approximation to reality. Nevertheless, the interpolation theory at least does not invalidate the use of the inversion technique in this case.

These conclusions settle a problem raised by Honig and Reyerson (13). The authors showed that if the inversion procedure of Sips (19) is applied to the data plotted in Figs. 1–3, one obtains three different distribution functions. In particular, the rutile surface seemed to present an abundance of high energy sites toward nitrogen, but not toward oxygen or argon. Presumably, if the concept of energy heterogeneity has physical reality, the distribution functions obtained with the three gases on the same solid should have been similar. The interpolation theory now indicates that the restrictive assumptions basic to the inversion procedure do not hold for the oxygen or argon isotherms. Hence, in the light of information now available, the energy distributions calculated in (13) from the latter two isotherms have no physical significance.

Perhaps one of the most interesting results is that the interpolation theory confirms the suitability of using nitrogen gas for surface area measurements of rutile according to the BET procedure. The selection of oxygen or argon as the adsorbate at 77° K. by Brunauer, Emmett, and Teller would obviously have been much less satisfactory for surface area studies. The interpolation method also indicates that the magnitude for n_m obtained by the BET method must be approximately correct. For, it may be assumed that the failure of the nitrogen datum points to lie within the area A of Fig. 1 is due primarily to the onset of multilayer formation. Hence, the fact that the points C and M agree within 10% lends credence to the BET results.

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THE ENTROPIES OF IONS IN AQUEOUS SOLUTION

I. DEPENDENCE ON CHARGE AND RADIUS[1]

By K. J. Laidler

ABSTRACT

Empirical equations recently proposed for the entropies of ions in aqueous solution involve a linear dependence on the first power of the valency z and, in some cases, an inverse dependence on the square of a modified radius. Such relationships have no fundamental validity since the entropies are related arbitrarily to a zero value for the proton. It is shown that the entropy changes for reactions of various ionic types indicate that the entropy must depend on z^2, as proposed by Born on the basis of simple electrostatic theory. When the entropies of monatomic ions are related to the absolute scale, in which the proton has a value of −5.5 e.u., they are found to vary linearly with z^2/r_u, where r_u is the univalent radius defined by Pauling. The slope is found to be close to that predicted by the Born equation, and the non-electrostatic part of the entropy is shown to correspond to the movement of the ion in a free volume of 0.73 cu. Å.

INTRODUCTION

Recently several workers (12, 9, 3, 4, 6) have proposed empirical equations which accurately relate the conventional partial molal entropies of ions in aqueous solution to parameters such as the valency, z, the effective radius, r_e, and, in the case of complex ions, the number of ligands. The prototype of such equations is that of Powell and Latimer (12) who show that the entropies of monatomic ions are accurately represented by the formula

$$[1] \qquad \bar{S}^\circ = (3/2)\, R \ln(\text{at.wt.}) + 37 - 270\, z/r_e^2$$

where the effective radius r_e is the crystal radius plus 2.0 Å in the case of cations and 1.0 Å in the case of anions. The discussion that follows will relate explicitly to the Powell–Latimer scheme but the arguments are applicable, *mutatis mutandis*, to all of the others.

DEPENDENCE OF ENTROPY ON CHARGE

Although it is undoubtedly the case that the equations permit accurate estimates to be made of the entropies of ions of various kinds, they unfortunately do not correctly represent the manner in which entropies depend upon charge and radius. That this is the case becomes apparent from a consideration of the following points:

(1) The entropies employed in the empirical equations are arbitrarily related to the value of zero for the proton. Gurney (8) has recently obtained convincing evidence that the absolute entropy of the proton is actually −5.5 e.u., and if this is the case the entropies of ions of various types must all be modified by the subtraction of $5.5z$ in the case of cations and the addition of $5.5z$ in the case of anions. With these changes Powell and Latimer's straight line plot splits into several parallel straight lines, and a different dependence of $\bar{S}^\circ$ on z is clearly called for.

[1]*Manuscript received April 24, 1956.*
Contribution from the Department of Chemistry, University of Ottawa, Ottawa, Canada.

(2) Born (2) has proposed that the free energies and entropies of ions are the values given by simple electrostatic theory for a conducting sphere of charge ze and radius r. The resulting expressions, and the numerical values corresponding to ions in aqueous solution at 25° C., are

$$[2] \qquad F^\circ_{el} = z^2e^2/2r\,D = 2.05\,z^2/r \text{ kcal. per mole,}$$

$$[3] \qquad S^\circ_{el} = (z^2e^2/2r\,D)\,(\delta \ln D/\delta\,T) = 9.42\,z^2/r \text{ cal. per degree.}$$

(In using the above numerical coefficients, the value of r must be in Å.) On the basis of Eq. [3] one would expect a linear dependence of $\bar{S}^\circ$ on z^2/r, rather than upon z/r_e^2 as found by Powell and Latimer. This is not, of course, a compelling argument, since Born's assumption that ions behave like conducting spheres may not be justified. However it will now be shown that there is strong *experimental* evidence in favor of a dependence on z^2.

(3) Since the variation of entropy with charge is much more important than the variation with size (and this is especially true of the absolute entropies) one can, to a rough approximation, ignore size effects and see how entropy changes in complete reactions depend on the charges on the ions. Thus if one considers a reaction

$$A^{z_A} + B^{z_B} \rightleftarrows C^{z_C} + D^{z_D}$$

the entropy change, if the individual entropies depend on z^2, will be related to the quantity

$$z_C^2 + z_D^2 - z_A^2 - z_B^2$$

which may be written as $\sum z^2$. If on the other hand the entropies depend on z the entropy change will be related to

$$z_C + z_D - z_A - z_B$$

which will be written as $\sum z$. There are a number of reactions for which $\sum z^2$ and $\sum z$ differ in sign, and these should provide a means of differentiating between the two possibilities; apart from this, one can see whether trends in ΔS can be correlated with $\sum z^2$ or with $\sum z$.

The results for a number of reactions are shown in Table I. The ΔS values were mostly calculated using the $\bar{S}^\circ$ values listed by Latimer; these $\bar{S}^\circ$ values are all conventional ones, based on $\bar{S}_{H^+}^\circ = 0.0$, but the values of ΔS are absolute and do not depend on this convention. Only a selection of possible examples can be given, but those chosen are typical and show the general trends. It is clear that there is a close correlation between ΔS and $\sum z^2$, but none at all between ΔS and $\sum z$. Fig. 1 shows a plot of ΔS against $\sum z^2$. If attempts were made to predict ΔS on the basis of $\sum z$, the wrong sign would be obtained in many cases (e.g. reactions 11 to 14). One could, however, make rough estimates of ΔS by multiplying $\sum z^2$ by about 10.

This close correlation between ΔS and $\sum z^2$, covering a wide range of reaction types, and the lack of correlation with $\sum z$, strongly indicates that entropy is a function of z^2 and not of z. If the relationships proposed by Powell and

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TABLE I

ENTROPY CHANGES FOR REACTIONS OF VARIOUS IONIC TYPES

Reaction	$\sum z$	$\sum z^2$	ΔS (e.u.)	Ref.
1. $C_6H_5OH + OH^- \rightarrow C_6H_5O^- + H_2O$	0	0	− 8.2	10
2. $C_6H_5NH_2 + H_3O^+ \rightarrow C_6H_5NH_3^+ + H_2O$	0	0	1.4	10
3. $2H_2O \rightarrow H_3O^+ + OH^-$	2	2	− 18.7	9, 10
4. $NH_4OH \rightarrow NH_4^+ + OH^-$	2	2	− 18.9	9
5. $H_2CO_3 + H_2O \rightarrow H_3O^+ + HCO_3^-$	2	2	− 22.9	9
6. $HSO_4^- + H_2O \rightarrow H_3O^+ + SO_4^{2-}$	2	4	− 26.3	9
7. $HCO_3^- + H_2O \rightarrow H_3O^+ + CO_3^{2-}$	2	4	− 35.0	9
8. $HPO_4^= + H_2O \rightarrow H_3O^+ + PO_4^{3-}$	2	6	− 43.0	9
9. $UOH^{3+} \rightarrow U^{4+} + OH^-$	2	8	− 52.0	1
10. $ClO_4^- + 2H^+ + 2Fe^{2+} \rightarrow ClO_3^- + H_2O + 2Fe^{3+}$	0	8	− 73.5	9
11. $MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$	−2	20	−213.6	9
12. $Cr_2O_7^{2-} + 3Tl^+ + 14H^+ \rightarrow 2Cr^{3+} + 3Tl^{3+} + 7H_2O$	−4	24	−248.6	9
13. $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$	−4	30	−339.2	9
14. $2MnO_4^- + 5Tl^+ + 16H^+ \rightarrow 2Mn^{2+} + 5Tl^{3+} + 8H_2O$	−4	30	−359.2	9

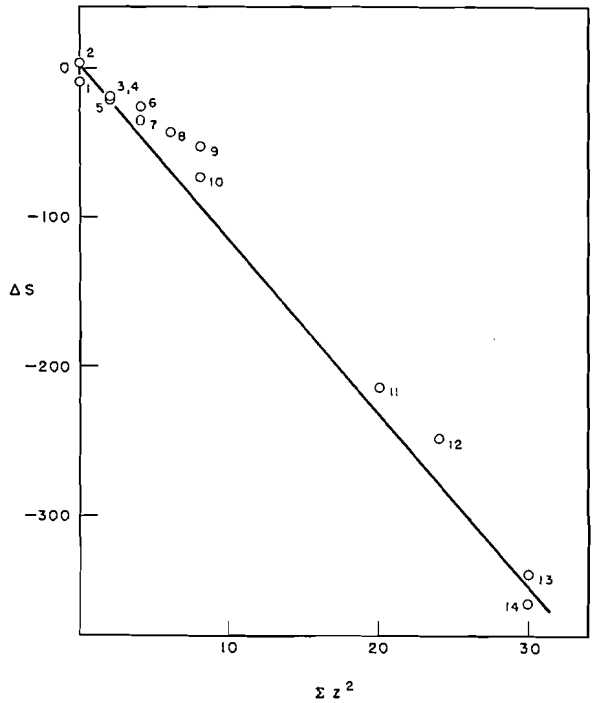

FIG. 1. Plot of entropy change against $\sum z^2$ for reactions of various ionic types. The numbers relate to the reactions listed in Table I.

Latimer were accepted as of fundamental significance it would be necessary to regard the correlations shown in Fig. 1 as purely coincidental, arising from fortuitous variations in ion radii. Such would appear to be extremely unlikely.

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A NEW EMPIRICAL EQUATION

In view of these conclusions it is clearly of interest to examine the absolute entropies of aqueous ions with a view to confirming their dependence on z^2 and to finding out how they vary with ion size.

Column 2 of Table II shows values for monatomic cations,* calculated from Latimer's values in the manner indicated above. In the next column the value $(3/2)R$ ln(at.wt.) has been subtracted from the absolute values. This procedure was found by Powell and Latimer to improve the correlation, and

TABLE II

ABSOLUTE ENTROPIES AND UNIVALENT RADII

Ion	$\bar{S}^\circ_{abs}$ ($H^+ = -5.5$)	$\bar{S}^\circ_{abs} - (3/2)\ R \ln$(at.wt.)	Univalent radius (Å)
Cs^+	26.3	11.8	1.69
Rb^+	24.2	9.0	1.48
K^+	19.0	8.1	1.33
Na^+	8.9	− 0.4	0.95
Ag^+	12.2	− 1.7	1.26
Li^+	− 2.1	− 7.9	0.60
Ra^{2+}	2	− 14.1	1.7*
Ba^{2+}	− 8	− 22.7	1.53
Hg^{2+}	− 16.4	− 32.2	1.25
Cd^{2+}	− 25.6	− 32.8	1.14
Sr^{2+}	− 20.4	− 33.7	1.32
Ca^{2+}	− 24.2	− 35.2	1.18
Mg^{2+}	− 39.2	− 48.7	0.82
Zn^{2+}	− 36.5	− 48.9	0.88
Tl^{3+}	− 58.5	− 74.3	1.15
In^{3+}	− 78.5	− 92.6	1.04
Al^{3+}	− 91.4	−101.2	0.72
Ga^{3+}	− 99.5	−112.1	0.81
U^{4+}	−100	−116.3	1.6*
Pu^{4+}	−109	−125.3	1.3*

Estimated by extrapolation.

was found to do the same in the present study; its theoretical justification is considered below. Column 4 shows the "univalent" radii r_u given by Pauling (11); these were found empirically to give better correlation than the ordinary crystal radii. This is understandable in view of the fact that the univalent radii represent the true sizes of the ions, whereas the crystal radii are reduced to various degrees owing to electrostatic attractions.

In order to confirm the dependence of $\bar{S}^\circ_{abs}$ on z^2 one may plot $\bar{S}^\circ_{abs} - (3/2)\ R \ln$(at.wt.) against $1/r_u$ and find by interpolation the entropies corresponding to some arbitrary radius. Taking 1.3 Å as the radius, the entropies obtained are as follows: $z = 1$, 7.5 e.u.; $z = 2$, −27.0 e.u.; $z = 3$, −68 e.u.; and $z = 4$, −126 e.u. These values are shown plotted against both z and z^2 in Fig. 2. The linear dependence on z^2 is clearly established.

Since Eq. [3] predicts a dependence of entropy on z^2/r, it is natural to test such a dependence first. Fig. 3 shows a plot of $\bar{S}^\circ_{abs} - (3/2)\ R \ln$(at.wt.) against z^2/r_u. The linearity shown in this plot is as good as could be expected;

Anions are not considered in this paper, since the range of values is not sufficiently great to permit a test of the dependence on z and r.

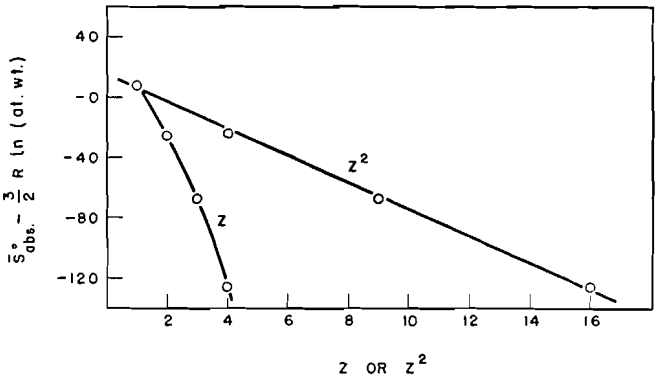

FIG. 2. Plot of $\bar{S}°_{abs} - (3/2)\,R\ln(at.wt.)$ against z (the valency) and z^2, the entropies corresponding to a univalent radius of 1.3 Å. This plot establishes the fact that entropy varies linearly with z^2 and not with z.

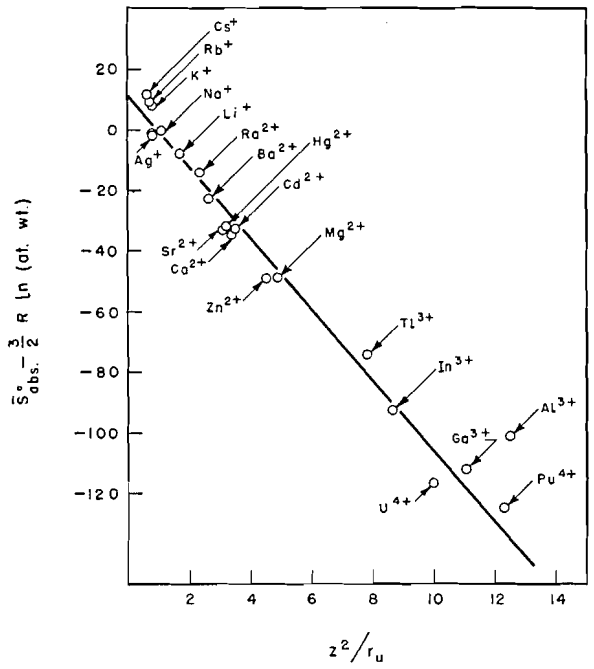

FIG. 3. Plot of $\bar{S}°_{abs} - (3/2)\,R\ln(at.wt.)$ against z^2/r_u, where z is the valency and r_u the univalent radius.

some improvement could be realized by adding a small constant value to all of the radii, but is hardly worth while in view of uncertainties in the univalent radii. It may be noted that small errors in the radii are highly magnified when z is large; an increase of 0.1 in the value for plutonium, for example, displaces the point by 0.9 to the left, and puts it to the left of the curve.

The only point that is seriously off the line is that for aluminum. This may well be due to an error in the radius, and it is of interest that Goldschmidt (7)

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gave a crystal radius (0.83 Å) that is considerably greater than Pauling's value (0.5 Å). The use of a univalent radius calculated from Goldschmidt's value would displace the point to the left of the line. Apart from this case Goldschmidt's and Pauling's values are mainly in good agreement; for lithium, however, Goldschmidt's value is again larger than Pauling's, and the change would displace the point away from the line.

Attempts to find linear relationships using the crystal radii r_c rather than the univalent radii were not quite as successful. The addition of constant values to the crystal radii gave no advantage, and the use of functions like z^2/r_u^2, $z^2/(r_u+a)^2$, z^2/r_c^2, and $z^2/(r_c+a)^2$ showed no improvement over z^2/r_u.

It is therefore concluded that the function z^2/r_u is the most satisfactory simple function. The equation of the straight line, obtained by the method of least squares (neglecting aluminum), is

$$[4] \qquad \bar{S}^\circ_{abs} = (3/2)\ R \ln(\text{at.wt.}) + 10.2 - 11.6\ z^2/r_u.$$

The mean deviation in entropy is 4.8 e.u., and the mean deviation in $1/r_u$ is 0.16; at a radius of 1.2 Å this corresponds to a deviation in radius of about 0.12 Å, which is probably close to the actual uncertainty.

DISCUSSION

Several points of interest arise from this empirical equation. In the first place, the coefficient of the z^2/r_u term in Eq. [4] is not far from that given by Eq. [3]. It thus appears that as far as entropies are concerned the simple electrostatic picture is much nearer to the truth than had hitherto been suspected.

Other points relate to the significance of the term $(3/2)\ R \ln(\text{at.wt.})$ and to the intercept on the entropy axis. The contribution

$$[5] \qquad \bar{S}^\circ_{n.e.s.} = (3/2)\ R \ln(\text{at.wt.}) + 10.2$$

appearing in Eq. [4] is clearly the non-electrostatic part of the entropy. A very simple model (5) for a monatomic particle in the liquid phase regards it as having translational motion in a "free volume" v_f of the order of a molecular volume; the partition function corresponding to this type of motion is

$$[6] \qquad f = \{(2\pi mkT)^{3/2}/h^3\} v_f e^{-E_0/RT}$$

where E_0 is the difference in energy between the particle in the liquid phase and in the gas phase. If the ions are regarded as independent localized systems this partition function leads to the result that the entropy per mole is

$$[7] \qquad \bar{S}^\circ = R[3/2 + \ln\{(2\pi mkT)^{3/2} v_f/h^3\}].$$

This is equivalent to

$$[8] \qquad \bar{S}^\circ - (3/2)\ R \ln(\text{at.wt.}) = 3/2 + (3/2)\ R \ln\{(2\pi kT)/h^2N\} + R \ln v_f.$$

Insertion into this equation of the numerical values (with $T = 298.2°$ K.) gives rise to

$$[9] \qquad \bar{S}^\circ - (3/2)\ R \ln(\text{at.wt.}) = 2.91 + R \ln v_f$$

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where v_f is the free volume in cu. Å.

In comparing this equation with Eq. [5] it is necessary to take into consideration the fact that Eq. [5] contains a "cratic" term (8) for the mixing of the ions with water; this term amounts to $R \ln(1000/55.5) = 7.9$ e.u. In order for Eqs. [5] and [9] to be equivalent it is therefore necessary that

$$10.2-7.9 = 2.9+R \ln v_f. \qquad [10]$$

This leads to a value for v_f of 0.73 cu. Å, which is entirely reasonable. The volume should, of course, be smaller than the volume of the actual cavities occupied by the ions, owing to the volumes of the ions themselves.

The general conclusions to which the present work leads are therefore as follows. The absolute entropy of a monatomic ion in solution can be regarded as made up of a non-electrostatic and an electrostatic term. The first of these corresponds to the free motion of the ion in a free volume of about 0.73 cu. Å, and the electrostatic term is represented approximately by Eq. [3], which is based on classical electrostatic theory. The view that entropies depend on z seems to be entirely without foundation.

Later papers will deal more explicitly with the entropies of polyatomic ions.

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THE ADSORPTION OF NITROGEN BY BROMINATED GRAPHITE AND CARBON BLACK[1]

By H. L. McDermot and J. C. Arnell

ABSTRACT

The adsorption of nitrogen has been measured at 78° K. for three artificial graphites and one carbon black, which have been brominated to saturation and then debrominated by heat-treatment under vacuum or in the presence of an inert gas over a range of temperatures. During the bromine removal, the graphites were heated to a maximum temperature of 1000° C. and the carbon black to a maximum of 1200° C. When the graphite of smallest area was brominated it did not return to its original area even after heat-treatment at 1000° C., whereas the graphite of largest area exceeded its original area when it was brominated and heated at 1000° C. The surface area of the brominated carbon black was restored to the original value when it was evacuated at 400° C. After evacuation at 600° C., the surface area was greater than that of the original carbon black, but fell to a value less than the original area when the sample was evacuated at 1200° C. These observations are believed to be in accord with the known structures of the graphites and the carbon black.

INTRODUCTION

It has been known for a long time that graphite sorbs copious quantities of bromine when simply exposed to the vapor at room temperature. In 1933, Frenzel (2) found that graphite took up 83.5% of its own weight of bromine from an atmosphere saturated with bromine vapor. This observation was confirmed by Rüdorff (7) who undertook a systematic investigation of the sorption of bromine by a variety of natural graphites. He found that they all sorbed very nearly 83% of their own weight irrespective of the size of the graphite crystals. From this observation together with the large bromine sorption he concluded that bromine was not simply adsorbed on the surface of the crystals. Microscopic observation of single crystals of graphite revealed an expansion along the *c*-axis of the crystal accompanying bromination. X-ray diffraction photographs of the brominated graphite showed only 001 lines whose position indicated an identity period of 10.4 Å compared to an identity period of 3.35 Å for the untreated graphite. All of these experimental observations were explained by postulating that the bromine was intercalated between the sheets of hexagonally arranged carbon atoms which comprise the graphite crystal. Since the amount of bromine sorbed was independent of the size of the graphite crystals, it follows that virtually all the bromine was held in this fashion.

Following the work of Rüdorff, little work was done on the subject of brominated graphites. In particular, with the exception of an important investigation by Hennig (4), no work was done on the properties of the product remaining after debromination of the graphite. This product, which is a graphite containing a small amount of firmly held bromine, has been called a "residue compound" by Hennig (4). He has shown that the composition of

[1]*Manuscript received April 23, 1956.*
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these compounds is a function of the composition of the parent lamellar compounds and of the temperature to which the parent compound is heated during decomposition. Hennig measured the X-ray diffraction patterns of some of the residue compounds and found only a very slight increase in the *c* spacing of the graphite compared to that of the unbrominated graphite. He concluded from this that very little of the bromine of the residue compound was intercalated in the graphite. He suggests that it was trapped by crystal imperfections.

The work to be presented logically follows that done by Hennig. It is a systematic investigation of some of the adsorptive properties of residue compounds prepared from three artificial graphites and one carbon black. In particular, the surface area and hysteresis effects have been studied by measuring the adsorption of nitrogen at 78° K.

EXPERIMENTAL AND RESULTS

Three graphites and one carbon black were chosen for study. The graphites used were artificial graphites manufactured by Acheson Colloids Ltd. and have been described previously by McDermot and Arnell (5). For the purpose of this work, they have been designated as G-1, G-2, and G-3. The carbon black, designated as Spheron 9, was provided through the courtesy of the Godfrey L. Cabot Co. Some of its properties have been given by McDermot and Lawton (6). All the samples were brominated by exposure to saturated bromine vapor in the absence of air at room temperature. The surface areas of the graphites and of the carbon black prior to bromination and the approximate amounts of bromine sorbed by them are presented in Table I.

TABLE I

	Surface area, meters²/gm.	Weight of bromine sorbed, gm./gm.
G-1	45	0.6
G-2	96	—
G-3	18	0.6
Spheron 9	112	0.4

It will be noted that there is no correlation between the weights of bromine sorbed and the surface areas of the graphites. Moreover the amounts of bromine sorbed are considerably less than those reported by Rüdorff.

After bromination the residue compounds were prepared by evacuating the samples at a series of temperatures beginning at room temperature and continuing up to about 1000° C. After each period of heating the samples were cooled in liquid nitrogen and the nitrogen adsorption measured at 78° K. In some of the early experiments, equipment was not available for heating the samples to high temperatures *in vacuo* and therefore they were heated in a stream of inert gas. For completeness the adsorption of nitrogen was measured for one graphite while it was still saturated with bromine.

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The results for G–3 are presented first because most of the work was done with this graphite. The surface areas corresponding to different heat treatments are listed in Table II for three series of experiments carried out on this graphite.

TABLE II

Run	Treatment	Br_2 retained, gm./gm.	Surface area, meters²/gm.
1	Saturated with Br_2	0.6	5.2
	Evacuation at 100° C.	—	10.5
	Evacuation at 300° C.	0.07	9.8
2	Evacuation at 25° C.	0.068	8.6
	Evacuation at 100° C.	0.064	9.9
	Evacuation at 300° C.	0.055	10.1
	Evacuation at 600° C.	0	9.6
	Evacuation at 1000° C.	0	11.8
3	Saturated with Br_2 to only 0.24 gm./gm.		
	Evacuation at 25° C.	0.03	7.9
	Untreated graphite	—	18.4

Some of the results from Run 1 are plotted in Fig. 1 along with the isotherms of the untreated graphite. The isotherm measured after the 300° C. evacuation is omitted because it was almost identical to that for the 100° C. evacuation. Fig. 2 depicts the isotherms measured after evacuation of the sample at room temperature and after heating it to 1000° C.

In a previous paper dealing with these graphites (5), McDermot and Arnell demonstrated the existence of two types of hysteresis in the low temperature isotherms. The first type of hysteresis, which was believed to be due to the porous nature of the graphites, manifested itself as a broad hysteresis loop extending from saturation down to a relative pressure of approximately 0.45. This type of hysteresis has been called "pore" hysteresis. The second type of hysteresis, which was termed "swelling hysteresis", was attributed to intercrystalline swelling and was seen as an inability of the desorption curve to rejoin the initial adsorption curve below a relative pressure of 0.45, where "pore" hysteresis was manifestly impossible.

Both of these hysteresis effects are evident in the isotherms for nitrogen adsorbed on G-3. In the case of the graphite saturated with bromine, the isotherm was found to be reversible over the whole range of relative pressures as might be expected if it is assumed that the pore space and the space responsible for swelling are completely filled with bromine at saturation. Both types of hysteresis are absent. As bromine is removed from the saturated graphite the pores empty and the hysteresis loop, characteristic of the pore structure, reappears in the samples which have been evacuated at temperatures as low as 25° C. This is shown by the isotherm in Fig. 2 (triangles) measured after evacuation at room temperature. Swelling type hysteresis only reappears in the later stages of debromination where evacuation at high temperatures was used. In the case of G-3, swelling hysteresis was observed only after the sample had been heated to 1000° C. as is shown by the squares in Fig. 2.

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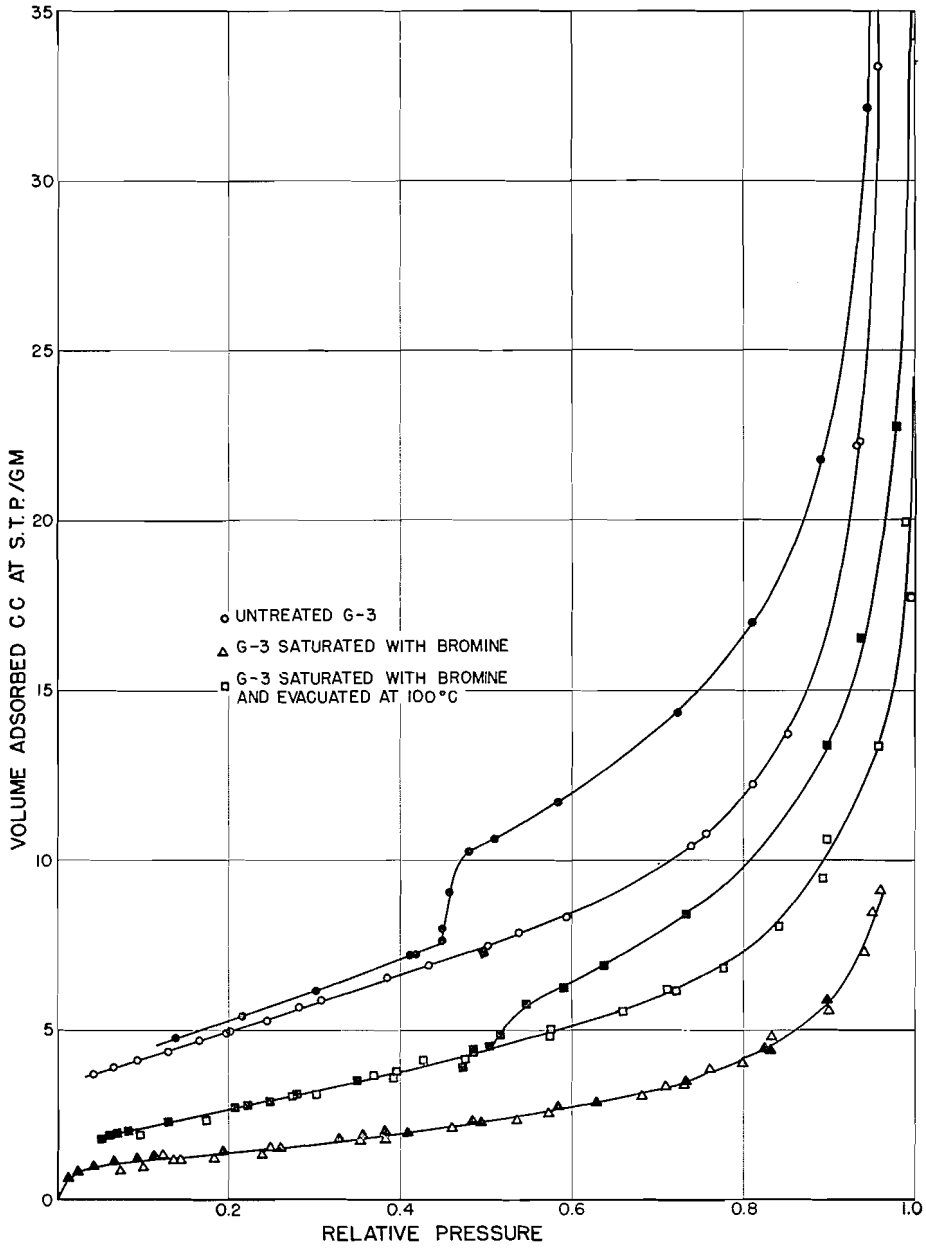

FIG. 1.

An experiment was conducted to ascertain the effect of partial bromination of a sample of G-3. The sample was brominated to a concentration of 0.24 gm. bromine/gm. graphite and then evacuated at room temperature to a bromine content of 0.033 gm./gm. The isotherm measured after this treatment is compared to one measured after room temperature evacuation of a fully bro-

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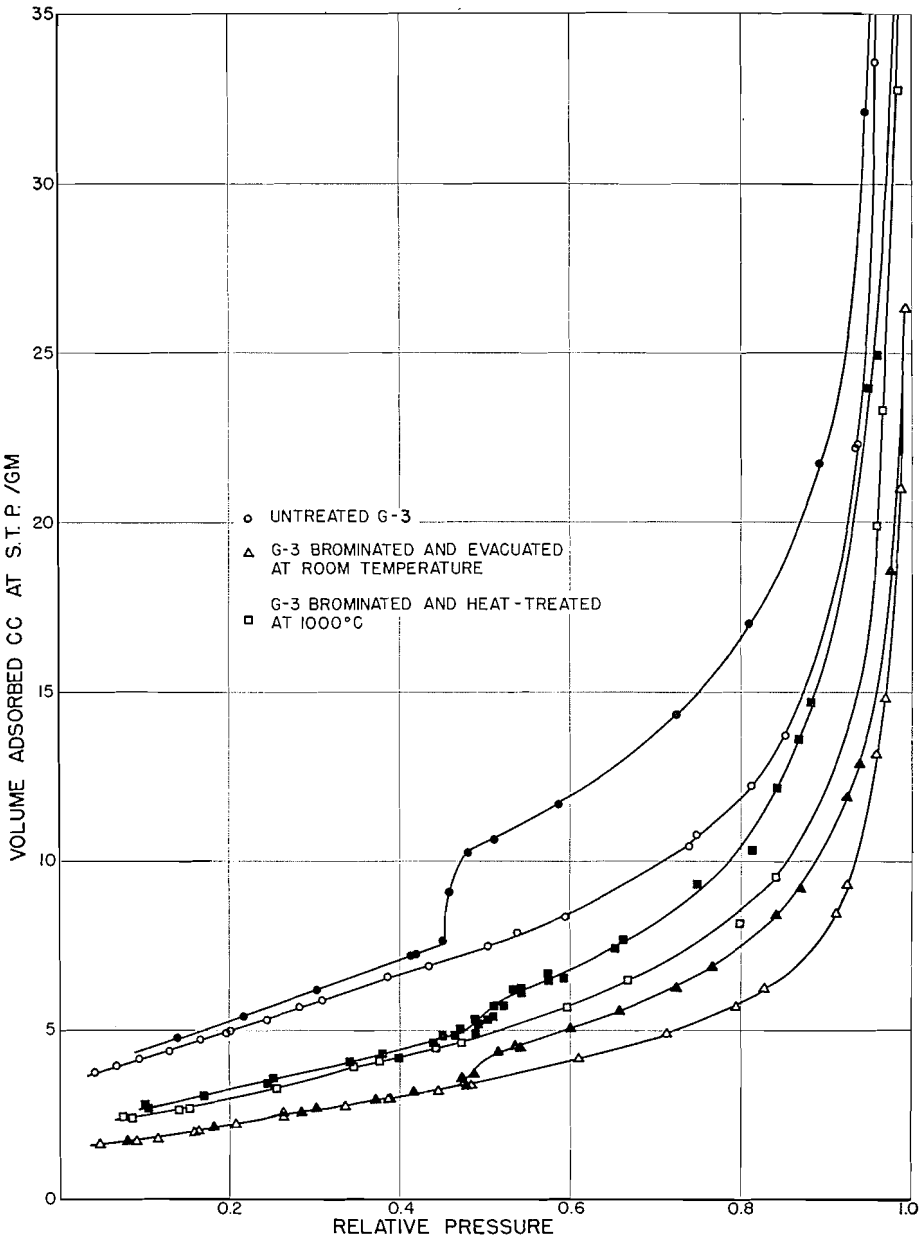

FIG. 2.

minated sample in Fig. 3. After evacuation at room temperature the bromine content of the saturated sample fell from 0.6 gm./gm. to 0.068 gm./gm. It is clear that the surface areas of the two samples are identical. It will be noted that the desorption curve obtained after evacuation of the partially brominated graphite is slightly higher than that measured after evacuation of the fully brominated sample. This is believed to be due to the fact that during

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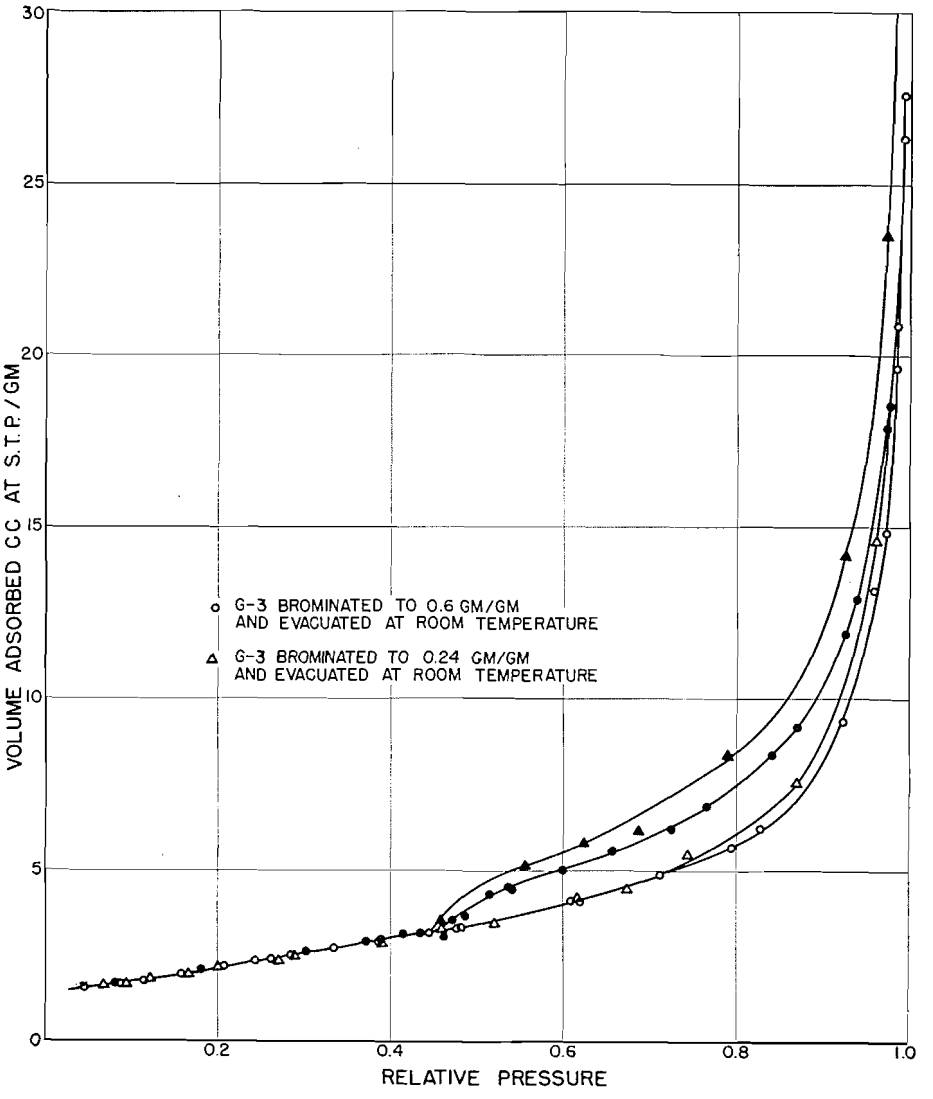

FIG. 3.

nitrogen adsorption a somewhat higher degree of saturation was reached in the former case than in the latter, rather than because of any difference in pore structure between the two samples.

The effect of bromination on G-1 is illustrated by the isotherms shown in Fig. 4. The isotherms were measured with a sample of G-1 which had been saturated with bromine, evacuated successively at room temperature and 200° C., and then heat-treated at 500° C. and 1000° C. For the sake of clarity the desorption points at the higher pressures are omitted because this part of the isotherm is similar in shape for all of the graphites and is illustrated by the isotherm following the 200° C. evacuation. The lower desorption points are included because they again point out that the so-called swelling hysteresis,

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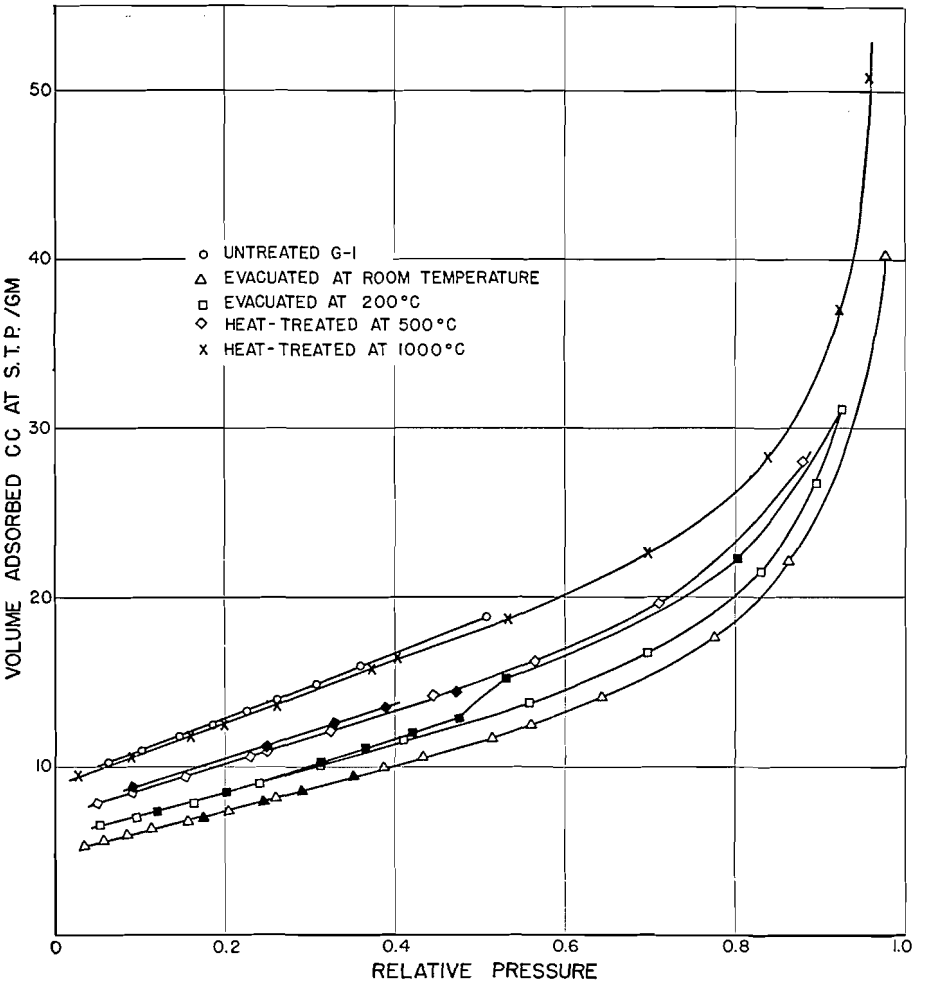

FIG. 4.

which is absent in the room temperature isotherm, becomes apparent in the 500° C. isotherm. It should be noted that unlike G-3, the surface area does return to almost its original value after the 1000° C. heating. The surface area corresponding to the various treatments along with the quantity of bromine retained by the graphite is given in Table III.

TABLE III

Treatment temperature, ° C.	Br_2 retained, gm./gm.	Surface area, meters²/gm.
25	0.03	27
200	0	32
500	0	37
1000	0	44
Untreated graphite		46

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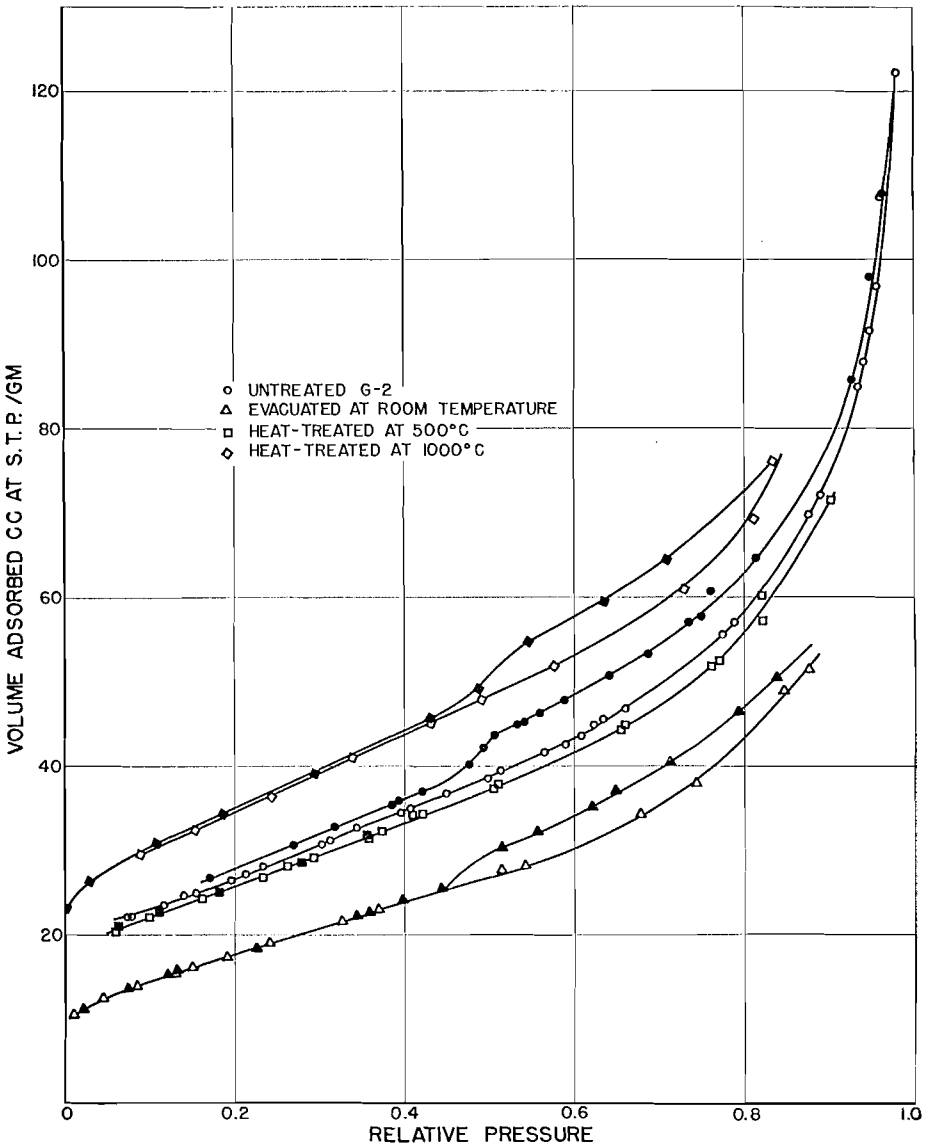

FIG. 5.

Isotherms were measured with a sample of G-2 which had been saturated with bromine, evacuated at room temperature, and then heat-treated at 500° C. and 1000° C. These isotherms along with that for the untreated graphite are presented in Fig. 5. For clarity many of the desorption points have been omitted. The most remarkable feature of these isotherms is the increase in surface area observed after the 1000° C. heat-treatment over that of the untreated graphite. This is also brought out in Table IV which gives the surface areas corresponding to different heat-treatments.

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TABLE IV

Treatment temperature, ° C.	Br_2 retained, gm./gm.	Surface area, meters²/gm.
25	0.09	70
500	0	92
1000	0	121
Untreated graphite		96

The increase in area over that of the original graphite which was observed after the 1000° treatment was quite different from the behavior of the graphites with smaller surface areas. Accordingly an experiment was done to ascertain that the increase was indeed characteristic of the brominated graphite and not of the graphite. A sample of G-2 was heated to 1000° C. for the same length of time as was used for the brominated compound. The isotherm was measured for this sample and is shown in Fig. 6 along with that for the untreated G-2.

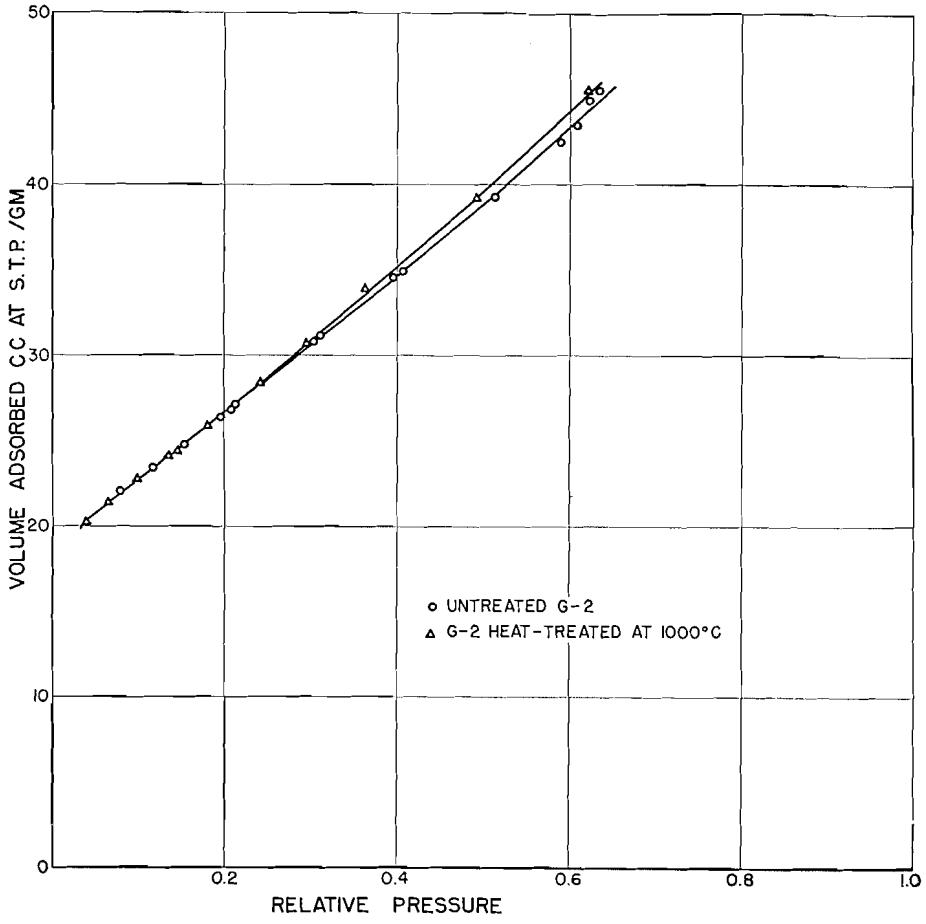

FIG. 6.

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It can be seen that there is little difference between the two isotherms.

Isotherms were measured for a sample of Spheron 9 which was brominated, evacuated successively at room temperature, 200°, and 400°, and then heat-treated at 600° and 1200° C. Representative isotherms are shown in Fig. 7

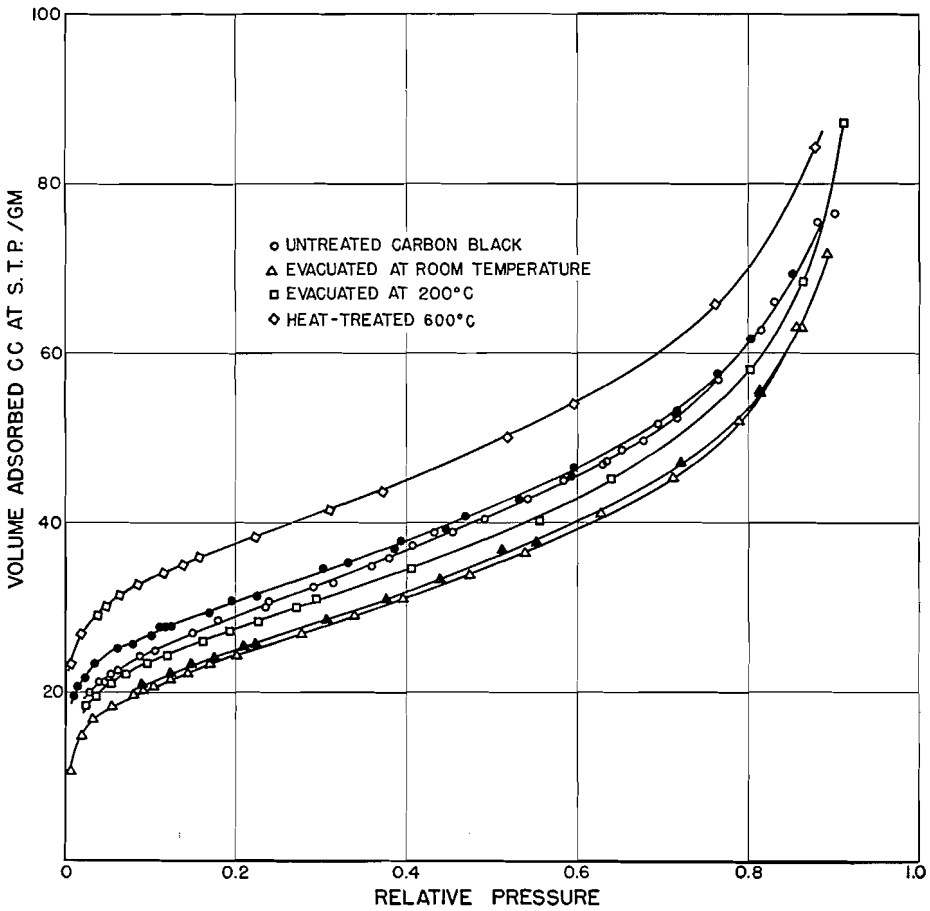

FIG. 7.

along with the isotherm of the untreated carbon black. All of the isotherms exhibited swelling hysteresis but this is only shown for one of the isotherms to avoid a confusion of points. It will be noted that this is the first carbon whose isotherms after room temperature evacuation have shown this type of hysteresis. The surface areas corresponding to various temperatures along with the amounts of bromine retained by the Spheron are given in Table V.

The table shows that the surface area increased to more than its original value at 600° C. and then with further heating to 1200° C. dropped to below its original value.

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TABLE V

Temperature, ° C.	Br_2 retained, gm./gm.	Surface area, meters²/gm.
25	0.345	89
200	0.091	98
400	0.026	102
600	0	131
1200	0	94
Untreated	—	104

DISCUSSION

In the initial stages of debromination all the graphites behaved the same way. The adsorptive behavior of a fully brominated graphite is illustrated by the isotherm shown in Fig. 1 for a sample of G-3 saturated with bromine. It is clear from the lack of hysteresis in this case that the bromine has filled the pores as well as the interstitial spaces which are believed to be responsible for swelling hysteresis. When the sample is evacuated at room temperature most of the bromine is removed, the surface area increases considerably, and part of the pore volume is emptied as is shown by restoration of the hysteresis loop. However, in all the graphites, the lower parts of the isotherms were still reversible after evacuation at room temperature showing that bromine continued to block the adsorption sites that were responsible for swelling hysteresis. McDermot and Arnell (5) have suggested that this so-called swelling hysteresis is due to a process of intercrystalline swelling. It is reasonable to suppose that the area between the crystallites responsible for this swelling was occupied by bromine and was thus denied to the nitrogen molecules. Hence the absence of swelling hysteresis and the cause for the loss of some of the surface area of the sample.

In the case of Spheron 9 the surface area measured by the low temperature nitrogen adsorption method is not the area of the crystallites, but of agglomerates of many crystallites. Moreover the crystallites of the carbon black are not regular crystals such as those of graphite but are more correctly parallel layer groups in which the orientation is random in an axis perpendicular to the layers of carbon atoms (1). Spheron 9 is not porous but it does display swelling type hysteresis (6). It is interesting to note in this connection that although the carbon black loses a considerable fraction of its original surface area on bromination and subsequent evacuation at room temperature, swelling hysteresis is still present in contrast to the behavior of the graphites. This point is shown very clearly by the isotherm outlined by the triangles in Fig. 7. Such behavior is remarkable because after evacuation at room temperature the carbon black retains more bromine than any of the graphites. McDermot and Lawton (6) have proposed that intercrystalline swelling is also responsible for the hysteresis effects that they have observed to accompany the adsorption of nitrogen by Spheron 9. Since the crystallites of the carbon black are compacted into agglomerates it is possible that spaces responsible for swelling hysteresis are of such a size that they may be penetrated by nitrogen molecules,

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but not by the much larger bromine molecules. Hence, swelling hysteresis appears for the sample after evacuation at room temperature despite the fact that a relatively large amount of bromine is retained by the carbon black.

It is of particular interest to examine in some detail the behavior of the graphites after evacuation at 1000° C. The graphite of lowest surface area G-3 loses area when it is brominated and never regains it entirely even when heated to 1000° C. By contrast G-2, which has the highest surface area, shows an increase in area with respect to its original area when it is brominated and heated to 1000° C. G-1, whose surface area lies between the other two, just reaches its surface area after heating to 1000° C. The behavior of the graphites would thus appear to be related to the surface area of the starting material. Wilson and McDermot (8) have taken X-ray diffraction photographs of two of the Acheson graphites, of which one was G-3, and showed that the line broadening is consistent with their nitrogen surface areas. Hence the surface area can be taken to be a measure of the crystallite dimensions, in which case G-3 has the largest crystallites and G-2 the smallest. Viewed in these terms it is clear that the loss in surface area on bromination and subsequent removal of bromine at high temperatures such as was observed for G-3 can only be explained by the filling of cracks or crevices by bromine or by crystallite growth. The first explanation would be expected to apply at low debromination temperatures because the bromine would be held by strong adsorptive forces which prevail in such fissures. However, it is reasonable to expect that a temperature of 1000° C. would suffice to drive off physically adsorbed bromine. Hence the loss of surface area after the high temperature treatment is likely due to crystallite growth resulting from the bromine and the high temperature treatments. In the case of G-2, the area of the brominated graphite which has been treated at 1000° C. is greater than that of the untreated graphite. By the same reasoning it must be assumed that the new surface area has been produced by a decrease in the average crystallite size due to an activation process resulting from the bromine and the heat-treatment. It has been proved experimentally that crystallite growth does not occur when G-2 is heated to 1000° C. (see Fig. 6); therefore, the activation process is not opposed by a tendency toward crystallite growth. Hence the difference in behavior between the graphites must be due to different susceptibilities towards crystallite growth and towards activation by bromine. Furthermore it would appear that these susceptibilities are related to the crystallite dimensions because it is only in this respect that the graphites differ appreciably from one to another.

It was observed that heat-treatment of brominated Spheron 9 at 600° C. produced a carbon black of much higher surface area than the original Spheron. This may have been caused by bromine activation at 600° C. which opened up new surface area for nitrogen adsorption. Further heating at 1200° C. diminished the area to a value slightly less than that of the parent carbon black. In this instance, it is likely that the heat-treatment caused some crystal growth with a consequent loss of surface area.

No attempt has been made in the course of this work to investigate the fully brominated compound in any detail. All of our attention has been focused on

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the residue compounds left after the evacuation of a brominated carbon. However it is noteworthy that contrary to the findings of Rüdorff (7), carbons of different crystallite dimensions sorbed different quantities of bromine. Rüdorff (7) and Frenzel (2) found that all their graphites sorbed 0.80 to 0.83 gm. of bromine/gm. of carbon. Goldsmith (3) reports a saturation value of 0.70 gm./gm. The values given in this paper range from 0.4 to 0.6 gm./gm. and do not bear any simple relationship to the area of the carbon. Thus it would appear that the quantity of bromine sorbed depends on the specific carbons and cannot be explained by any single process such as intercalation of bromine between the carbon planes. For example, in the graphites studied here, a part of the bromine was held in the pore structure and part was adsorbed on the surface. Judging by the ease with which most of the bromine could be removed, a large part was probably held by simple condensation between the particles. This idea is borne out by the observation that the powdered graphite, which was a free-flowing powder, became semisolid when saturated with bromine. This would be expected if the particles were stuck together by condensed liquid.

One experiment was done which showed that within the limits investigated the degree of bromination did not effect the surface area of the residue compound. A sample of G-3 which was only partially brominated yielded the same surface area after room temperature evacuation as a sample which had been saturated with bromine and then evacuated at room temperature, notwithstanding the fact that the quantities of bromine held by the two residue compounds were different. This is in accord with the notion that most of the bromine is held rather superficially and the only part that effects the surface area is that which is adsorbed or condensed between the crystallites.

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INTENSITY IN THE RAMAN EFFECT

V. THE EFFECT OF INTERMOLECULAR INTERACTION ON THE RAMAN SPECTRUM OF CARBON DISULPHIDE[1]

By J. C. Evans[2] and H. J. Bernstein

ABSTRACT

The Raman spectrum of CS_2 has been obtained photoelectrically for the liquid and solutions of varying concentrations in cyclopentane, and depolarization ratios and intensities measured. The intensity of the forbidden bands ν_2 and ν_3 relative to that of the Raman active band ν_1 decreases rapidly with dilution. The bands are present because of intermolecular interaction which probably occurs between the C atom of one molecule of CS_2 and only one of the S atoms of the other.

The Raman spectrum of liquid CO_2 has been investigated recently (9) and the doubly degenerate bending mode ν_2 and the antisymmetric stretching mode ν_3 which are forbidden by selection rules have been observed as weak bands along with the allowed totally symmetrical stretching mode ν_1. Although depolarization ratios of the forbidden bands were not measured it was argued from the band contours (9) in the liquid that ν_2 is depolarized and ν_3 polarized. These data have been interpreted on the basis of strong intermolecular interaction in liquid CO_2 which distorts the molecule along its length so that the center of symmetry is essentially destroyed (9).

One might expect a closely parallel situation with regard to spectral details and the effects of intermolecular interaction for carbon disulphide. In this paper we have investigated the Raman spectrum of CS_2, liquid and in solutions of cyclopentane, in order to establish—(i) that the presence of the forbidden bands in the Raman spectrum is indeed due to the environment and (ii) the effect of the interaction on the shape of the molecule.

The Raman spectrum of CS_2 (5), depolarization ratios (2), and relative intensities (6) have been obtained some years ago and the discussion of its spectrum and the effect of Fermi interaction given by Placzek (7) on the basis of these older data. Newer data have been compiled by Herzberg (4) and the positions of the bands given there are confirmed by our investigation to within ± 1 cm.$^{-1}$. For purposes of calculating resonance interaction constants the more accurately measured data quoted by Herzberg have been used. The depolarization ratios of the forbidden bands ν_2 and ν_3 have been measured confirming Bhagavantam's result (2) for ν_2 and ν_3 (polarized). For purposes of comparing frequencies the infrared spectrum of the liquid was also obtained.

EXPERIMENTAL

The Raman spectra were photoelectrically recorded on a White grating Raman spectrometer (10) using λ4358 as the exciting line. Depolarization ratios (ρ_{obs}) were measured by wrapping polaroid film around the Raman tube,

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Contribution from the Division of Pure Chemistry, National Research Council, Ottawa, Canada. Issued as N.R.C. No. 4018.
[2]*N.R.C. Postdoctorate Research Fellow 1953–55.*

first with its axis parallel to the tube and then at right angles, and these ratios corrected for convergence (8) to give ρ_{corr}. Integrated intensities were measured relative to the 458 cm.$^{-1}$ band of CCl_4 obtained under identical instrumental and optical conditions and were corrected for the spectral sensitivity of the photomultiplier $\sigma_{\Delta\lambda}$ and for convergence error according to [1]

$$[1] \qquad I_{true} = \left[\frac{I_{obs}(1+\rho_{corr})}{1+\rho_{obs}} \times \sigma_{\Delta\lambda} \Big/ \left\{ \frac{I_{obs}(1+\rho_{corr})}{1+\rho_{obs}} \times \sigma_{\Delta\lambda} \right\}_{458 cm.^{-1}} \right] \times 100$$

where 100 is taken as the true integrated intensity of the 458 cm.$^{-1}$ band in CCl_4.

When bands overlapped, no attempt to resolve them by curve analysis was made, the measured intensity being taken as the area under the contour. This is indicated by bracketing bands in the tables. The Raman spectra of three solutions of CS_2 in cyclopentane were also measured in which the ratio of the volume of CS_2 to the total volume was 0.65, 0.49, and 0.36. The infrared spectrum was obtained with a Perkin Elmer 12C double pass spectrometer using CsBr, KBr, and NaCl optics. The results for CS_2 liquid are given in Table I and the Raman spectrum shown in Fig. 1.

TABLE I
LIQUID CS_2

Assignment[a]	$\Delta\nu$[b]	Raman $\Delta\nu$	Raman ρ_{obs}	Raman ρ_{corr}	Raman I_{true}[d]	Infrared ν
ν_2		390	0.7_9	0.6_3[c]	9.7_3	393 s.
ν_1'	648.3	648	0.4_1	0.2_5	488	
ν_1	656.5	655				654 w.
$2\nu_2$	796.0	797	0.4_0	0.2_5	94.2	789 v.w.
$2\nu_2'$	804.9	804				809 v.w.
ν_3		1515	0.7_9	0.6_3	6.9_4	Not measured

[a] *ν_1' and $2\nu_2'$ are satellite lines corresponding to the transitions (11'0), (03'0) ← (01'0).*
[b] *Data from Herzberg, Ref. 4.*
[c] *Measured by Bhagavantam to be 0.8 (Indian J. Phys. 7: 83. 1932).*
[d] *The 458 cm.$^{-1}$ band of CCl_4 is 100.*

Rough decomposition of the overlapped doublets at ~650 and 800 cm.$^{-1}$ indicates that the band at 648 cm.$^{-1}$ contributes about one-third of the total intensity and 804 cm.$^{-1}$ contributes about two-fifths of the intensity in its doublet. The ratio of the areas under the doublets is then

$$I_{800}/I_{650} = 94.2/488 = 0.193$$

and a rough estimate of $I_{2\nu_2}/I_{\nu_1}$ is 0.17_4. These ratios are to be compared with 0.32 obtained photographically by Pienkowski (6).

The intensities of the doublets at 650, 800 cm.$^{-1}$ and the forbidden band at 390 cm.$^{-1}$ have been measured as functions of concentration and the results shown in Figs. 2, 3, and 4, respectively. It should be mentioned that depolar-

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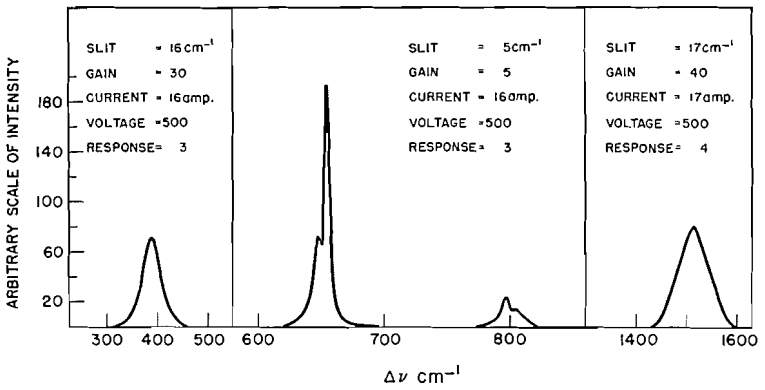

FIG. 1. Raman spectrum of liquid CS_2.

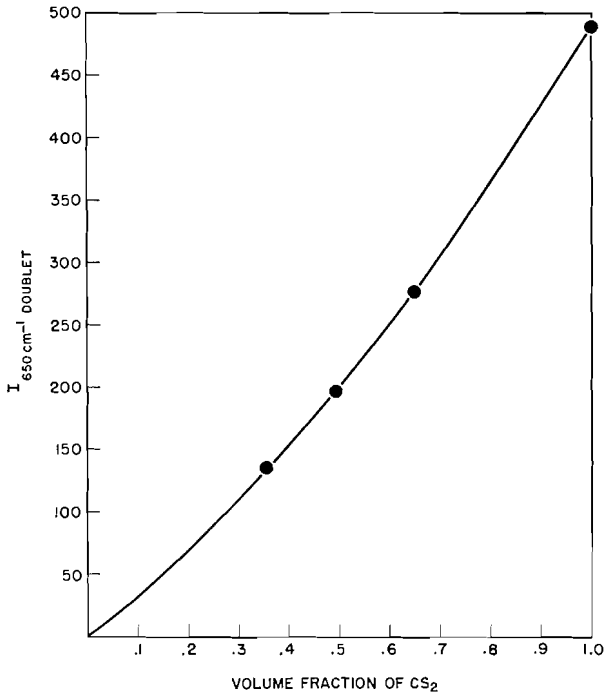

FIG. 2. Raman intensity of 650 cm.$^{-1}$ doublet of CS_2 as a function of concentration in cyclopentane.

ization ratios of the doublets and frequencies did not change within experimental error as a function of concentration, nor did the contours of the doublets at 650 and 800 cm.$^{-1}$. The ν_2 band position changed slightly as a function of concentration (from 390 cm.$^{-1}$ in CS_2 to 387 cm.$^{-1}$ in dilute solution) whereas the depolarization ratio was too uncertain to indicate whether or not changes in it took place. The depolarization ratio under most favorable conditions was very difficult to measure for the 390 cm.$^{-1}$ band because of overlapping (at

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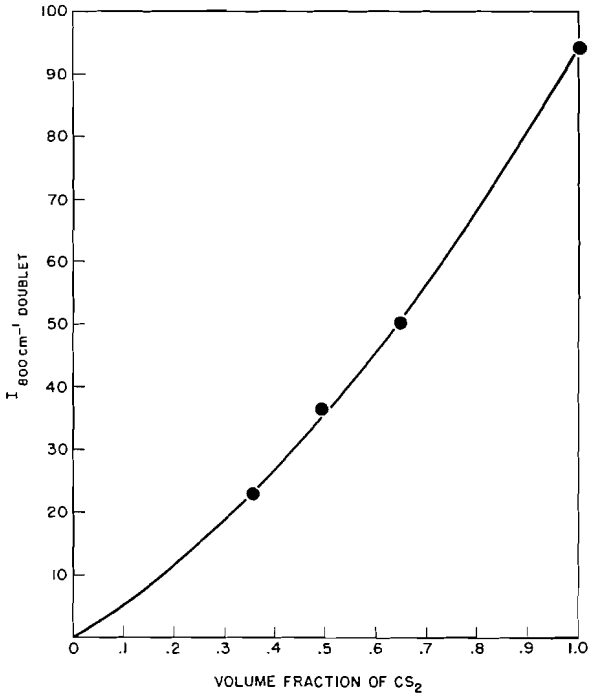

FIG. 3. Raman intensity of 800 cm.$^{-1}$ doublet of CS_2 as a function of concentration in cyclopentane.

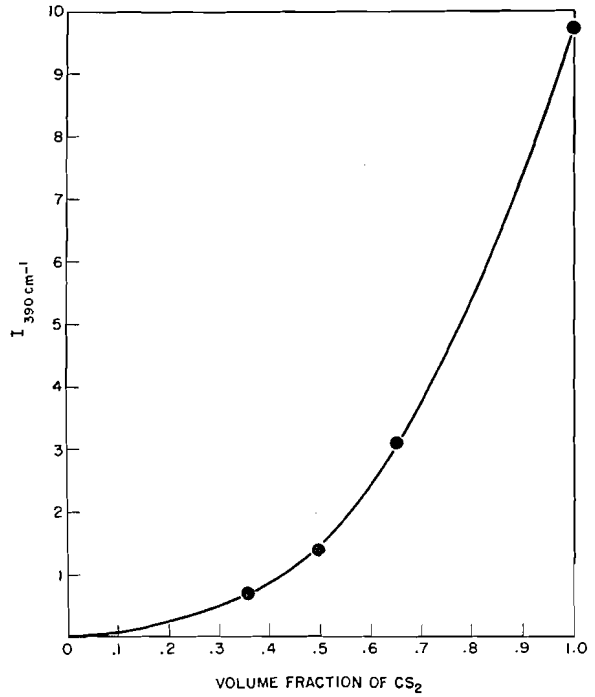

FIG. 4. Raman intensity of the band at 390 cm.$^{-1}$ in CS_2 as a function of concentration in cyclopentane.

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wide slits) with either the exciting line or the band at 650 cm.$^{-1}$ or both. The uncertainty in the quoted depolarization ratio may be as much as 0.15 for ν_2 whereas it is about 0.03 for the other bands.

DISCUSSION

From Placzek's formulae (7) for the separation of the main resonating components ν_1 and $2\nu_2$, viz. $X_1 = \sqrt{(\delta^2+4w^2)}$, and that for the satellites (ν_1' and $2\nu_2'$), viz. $X_2 = \sqrt{(\delta^2+8w^2)}$, we find, using the more accurate data quoted by Herzberg, that $\delta = 120.0$ cm.$^{-1}$ and $w = 35.6$ cm.$^{-1}$ for liquid CS_2. Further, according to the theory for resonance (5),

$$\frac{I_{2\nu_2}}{I_{\nu_1}} = \left(\frac{\sqrt{X_1-\delta}\,\alpha_1-\sqrt{X_1+\delta}\,\alpha_2}{\sqrt{X_1+\delta}\,\alpha_1+\sqrt{X_1-\delta}\,\alpha_2}\right)^2$$

where α_1 and α_2 are the polarizability derivatives for the transitions

$$(10^{\circ}0) \leftarrow (00^{\circ}0) \text{ and } (02^{\circ}0) \leftarrow (00^{\circ}0)$$

respectively. If $\alpha_2/\alpha_1 \ll 1$, which is usually true for the ratio of overtone to fundamental,

$$I_{2\nu_2}/I_{\nu_1} \approx (X_1-\delta)/(X_1+\delta) = 0.075_3.$$

The calculated value for this intensity ratio is about half the observed value. Using the approximate value for $I_{2\nu_2}/I_{\nu_1}$ obtained experimentally (0.17_4) and solving for α_2/α_1 gives -0.128 for this ratio. Since the uncertainty in the experimental intensity ratio is large, it is not even possible to say that the sign of the calculated ratio α_2/α_1 is correct. The negative sign would imply of course that either α_2 or α_1 was negative. Since the sum of the unperturbed levels $\nu_1^{\circ}+2\nu^{\circ}$ is the same as $\nu_1+2\nu_2 = 1452.5$ cm.$^{-1}$, and $2\nu_2^{\circ}-\nu_1^{\circ} = 120.0$ cm.$^{-1}$, we find that $2\nu_2^{\circ} = 786.2$ cm.$^{-1}$ and $\nu_1^{\circ} = 666.2$ cm.$^{-1}$ for liquid CS_2.

From Figs. 2, 3, and 4 we see that the bands at 650 and 800 cm.$^{-1}$ do not deviate as markedly from the linear concentration dependence as does the band at 390 cm.$^{-1}$. The deviation from linearity can arise not only from the effects of intermolecular interaction but also because of the dependence of the intensity on the refractive index and the reflection loss (1). If account is taken of these factors and the corrections indicated in Ref. 1 made, the result that the most marked intensity fall-off with concentration is experienced by the 390 cm.$^{-1}$ band is not altered. This would be expected if the presence of this band is due to intermolecular interaction. It is interesting to compare also the relative intensities of these bands as a function of concentration (see Table II).

It is evident from Table II that the relative intensity of the allowed doublets at 650 and 800 cm.$^{-1}$ remains approximately constant whereas the relative intensity of the 390 cm.$^{-1}$ band approaches zero with dilution. This is direct evidence that this band arises primarily from the action of the intermolecular force field. Buchheim (3) has shown that the ratio of the intensity of this forbidden band to that of the allowed band ν_1 should be proportional to the square of the field strength. If we assume a coulombic field between interacting CS_2 molecules, and that the distance between interacting molecules is

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TABLE II

Solution, vol. fraction of CS_2	Relative intensity*		
	390 cm.$^{-1}$	650 cm.$^{-1}$ doublet	800 cm.$^{-1}$ doublet
1.0	2.0_0	100	19.3
0.65	1.1_1	100	18.1
0.49	0.69	100	18.6
0.36	0.50	100	17.0

**The fourth power scattering term and the temperature dependent exponential term have not been included in the intensity.*

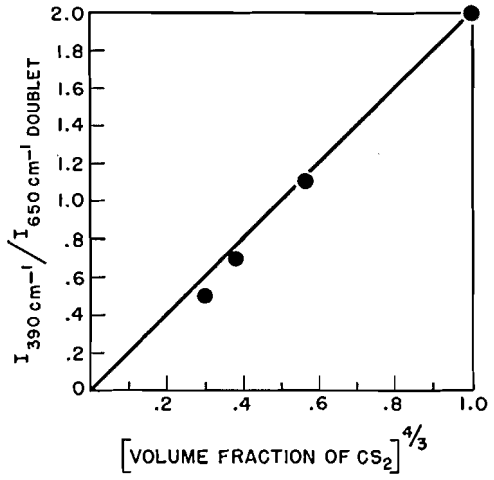

FIG. 5. Relative intensity of the 390 cm.$^{-1}$ band of CS_2 as a function of (concentration)$^{4/3}$.

proportional to the (molecular-volume)$^{1/3}$ then according to Buchheim the relative intensity of the 390 cm.$^{-1}$ band should be proportional to (volume-fraction)$^{4/3}$. This plot is shown in Fig. 5.

The reason the forbidden bands ν_2 and ν_3 appear in the Raman spectrum is to be found in the effects of the interaction field. In CO_2 the field distorted the molecule in the direction of the OCO axis giving essentially $C_{\infty v}$ symmetry (9) with its allowed Raman spectrum of two polarized (ν_1, ν_3) and one depolarized line (ν_2). In the case of CS_2 however both ν_3 and ν_2 are found to be polarized. This suggests that the distortion of the CS_2 molecule is such as to leave the molecule with a plane of symmetry only (C_s), in which case all three fundamentals are allowed in the Raman effect and should be polarized. This would imply not only distortion along the SCS axis but also at right angles to it.This would correspond to the interaction between CS_2 molecules taking place between a C atom of one molecule and only one of the S atoms of the other so that a real difference in field is experienced by the S atoms. Further, this difference is not only along the CS bond but also at right angles to it. On the basis of these spectroscopic data for liquid CS_2 and CO_2 one might expect the crystal structure of CS_2 to be different from that of CO_2.

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THE DIFFERENTIAL EQUATIONS OF CONSECUTIVE REACTIONS[1]

By A. E. R. Westman and D. B. DeLury

ABSTRACT

The differential equations of consecutive first-order reactions are formulated in a general manner. The solutions of these equations are shown to fall into a pattern, according to which the solutions to all such systems can be written down without resort to formal integration. The pattern is also convenient for making numerical calculations.

A SPECIAL CASE

Suppose that a molecule of tetraphosphate breaks down under hydrolysis to form one molecule of triphosphate and one of orthophosphate, that triphosphate breaks down into one molecule of pyrophosphate and one of orthophosphate, and that one molecule of pyrophosphate breaks down into two of orthophosphate. Let the symbols $\mathscr{A}$ $\mathscr{B}$ $\mathscr{C}$ $\mathscr{D}$ refer to these phosphates and let α, β, γ, δ stand for the numbers of phosphorous atoms in them ($\alpha = 4$, $\beta = 3$, $\gamma = 2$, $\delta = 1$). Let a, b, c, d ($a+b+c+d = 1$) represent the proportions of the phosphorus atoms, at time t, which are present as $\mathscr{A}$ $\mathscr{B}$ $\mathscr{C}$ $\mathscr{D}$ and let a_0, b_0, c_0, d_0 represent their values when $t = 0$. Then, if the reactions are first order and independent of each other and if their rate constants A, B, C* are known, the proportions a, b, c, d at any time t are defined by the following system of differential equations:

[I]
$$(1) \quad -da/dt = Aa,$$
$$(2) \quad -db/dt = Bb-(\beta/\alpha)Aa,$$
$$(3) \quad -dc/dt = Cc-(\gamma/\beta)Bb,$$

with initial conditions $a = a_0$, $b = b_0$, $c = c_0$, $d = d_0$ when $t = 0$. The value of d can be specified either by a differential equation or more simply by the relation

$$d = 1-a-b-c.$$

With a view to generalization later on, the symbol $(\mathscr{P}\mathscr{Q})$ will be introduced here to stand for the fraction of the phosphorus lost to $\mathscr{P}$ that goes directly into $\mathscr{Q}$. In terms of these symbols, the reaction described above is specified by

$$(\mathscr{A}\mathscr{B}) = \beta/\alpha, \quad (\mathscr{A}\mathscr{C}) = 0, \quad (\mathscr{A}\mathscr{D}) = 1-(\beta/\alpha);$$
$$(\mathscr{B}\mathscr{C}) = \gamma/\beta, \quad (\mathscr{B}\mathscr{D}) = 1-(\gamma/\beta);$$
$$(\mathscr{C}\mathscr{D}) = 1.$$

The ratios β/α and γ/β in Equations [I] will be replaced by $(\mathscr{A}\mathscr{B})$ and $(\mathscr{B}\mathscr{C})$.

The explicit solution of a set of equations like [I] offers no mathematical difficulty, but the resulting formulae are elaborate and cumbersome and offer too many opportunities for mistakes in calculation. The purposes of this note

[1]*Manuscript received April 27, 1956.*
Contribution from the Department of Chemistry and the Department of Mathematical Statistics, Ontario Research Foundation, Toronto 5, Ontario.
**Symbols A, B, etc., have been used to represent rate constants, instead of the conventional symbols k_A etc., to make the symmetry of the equations more apparent.*

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are to put forward an orderly notation for writing the solutions and to point out that, once the underlying pattern of the solutions is perceived, the solutions may be written down directly without resort to formal integration of the differential equations.

Direct integration of Equation (1) yields the solution

$$a = a_0 e^{-At},$$

which will be rewritten in the form

$$a = -a_0(1-e^{-At})+a_0.$$

Again, integration of Equation (2) produces the formula

$$b = a_0\left[-(\mathscr{A}\mathscr{B})\frac{A}{A-B}e^{-At}+(\mathscr{A}\mathscr{B})\frac{A}{A-B}e^{-Bt}\right]+b_0e^{-Bt},$$

which will be rearranged in the form

$$b = a_0\left[(\mathscr{A}\mathscr{B})\frac{A}{A-B}(1-e^{-At})-(\mathscr{A}\mathscr{B})\frac{A}{A-B}(1-e^{-Bt})\right]-b_0(1-e^{-Bt})+b_0.$$

Solutions for c, d, . . . can be expressed in the same manner, but the formulae soon become extremely elaborate. It is suggested here that a form of matrix notation simplifies the statements of these formulae and provides a pattern for writing directly the solutions to any such system of equations. One convenient scheme is the following. Write in a column the arguments $1-e^{-At}$, $1-e^{-Bt}$, etc., and finally, 1. Write in a row the initial amounts a_0, b_0, . . . , as shown in Table I. Then the cell of the table corresponding to an argument and an initial amount receives the appropriate multiplier.

The full pattern of the solution can be seen in the formula for c. The column of multipliers corresponding to a_0 all have the coefficient $(\mathscr{A}\mathscr{B})(\mathscr{B}\mathscr{C})$ which reflects the route by which a_0 has contributed to c. Likewise, they all contain the product of the rate constants AB, the two rates which are associated with this path. The denominators are selections from the differences $A-B$, $A-C$,

TABLE I

		a_0	b_0	c_0
a	$1-e^{-At}$	-1		
	1	1		
	$1-e^{-At}$	$+(\mathscr{A}\mathscr{B})\frac{A}{A-B}$		
b	$1-e^{-Bt}$	$-(\mathscr{A}\mathscr{B})\frac{A}{A-B}$	-1	
	1		1	
	$1-e^{-At}$	$-(\mathscr{A}\mathscr{B})(\mathscr{B}\mathscr{C})\frac{AB}{(A-B)(A-C)}$		
c	$1-e^{-Bt}$	$+(\mathscr{A}\mathscr{B})(\mathscr{B}\mathscr{C})\frac{AB}{(A-B)(B-C)}$	$+(\mathscr{B}\mathscr{C})\frac{B}{B-C}$	
	$1-e^{-Ct}$	$-(\mathscr{A}\mathscr{B})(\mathscr{B}\mathscr{C})\frac{AB}{(A-C)(B-C)}$	$-(\mathscr{B}\mathscr{C})\frac{B}{B-C}$	-1
	1			1

$B-C$, all taken according to the order of the sequence. The denominator in the multiplier of $1-e^{-At}$ is the product of those differences in which A appears, that of $1-e^{-Bt}$ is the product of those in which B appears, and so on. Lastly, the signs are alternately plus and minus, *starting with a minus sign at the foot of the column*. Similar observations apply to the b_0 column. The final column always consists simply of the -1 and 1.

Application of these rules provides the solutions to any such system of equations provided the conditions $(\mathscr{A}\mathscr{C}) = 0$, etc. are met. A useful check when the multipliers are being calculated numerically is provided by the fact that the multipliers must sum to zero in each cell. This is easily demonstrated algebraically and corresponds to the fact that, as t goes to infinity, the proportions of $\mathscr{A}, \mathscr{B}, \mathscr{C}$ etc. go to zero. (This must be modified if a rate constant is zero. See Appendix II.)

If, as an alternative to the assumption which led to System I, it is assumed that tetraphosphate hydrolyzes directly into pyrophosphate, which in turn breaks down into orthophosphate, System I must be replaced by another set of differential equations whose solutions are not included among those of System I. The solutions to the new system can, of course, be written out, but it seems worth while to lay out a general system of differential equations which includes as special cases those already mentioned and many others and to develop a rule for writing the solutions to the general system.

THE GENERAL SYSTEM

A reaction in which each of a sequence of substances $\mathscr{A}, \mathscr{B}, \mathscr{C}, \mathscr{D}, \ldots$ breaks down to form some or all of the substances which follow it in the sequence, but not those which precede it, will be termed a consecutive reaction. In terms of the symbols and assumptions introduced earlier, the differential equations for this reaction are

$$\text{[II]} \qquad \begin{aligned} (1) \quad -da/dt &= Aa, \\ (2) \quad -db/dt &= Bb-(\mathscr{A}\mathscr{B})Aa, \\ (3) \quad -dc/dt &= Cc-(\mathscr{A}\mathscr{C})Aa-(\mathscr{B}\mathscr{C})Bb, \end{aligned}$$

and so on.

The pattern for writing the solutions to System II is easily built up from the rules developed for System I. Equations (1) and (2) are the same in both systems, but Equation (3) in System II includes a term which provides for the path $\mathscr{A} \rightarrow \mathscr{C}$. The contribution from this path is provided for in the solution by the rule given earlier for a path like $\mathscr{A} \rightarrow \mathscr{B}$, with $\mathscr{B}$ replaced by $\mathscr{C}$ and B by C. The a_0 column in the formula for c is shown in Table II.

Once the solutions to the general system are written out, they may be reduced to any special case by giving the appropriate values to the symbols $(\mathscr{A}\mathscr{B})$, etc. and, when necessary, to the rate constants. For example, the situation tetra- $\rightarrow$ pyro- $\rightarrow$ ortho-, tri- $\rightarrow$ pyro-+ortho-, mentioned above, is specified by the values

$$\begin{aligned} (\mathscr{A}\mathscr{B}) &= 0, & (\mathscr{A}\mathscr{C}) &= 1, & (\mathscr{A}\mathscr{D}) &= 0; \\ & & (\mathscr{B}\mathscr{C}) &= \gamma/\beta, & (\mathscr{B}\mathscr{D}) &= 1-(\gamma/\beta); \\ & & & & (\mathscr{C}\mathscr{D}) &= 1. \end{aligned}$$

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COMPLETE FORMULA FOR d, GENERAL SYSTEM

	a_0				b_0	c_0	d_0
$1-e^{-At}$	$+(\mathscr{A},\mathscr{B})(\mathscr{B},\mathscr{C})(\mathscr{C},\mathscr{D})\frac{ABC}{(A-B)(A-C)(A-D)}$	$-(\mathscr{A},\mathscr{B})(\mathscr{B},\mathscr{D})\frac{AB}{(A-B)(A-D)}$	$-(\mathscr{A},\mathscr{C})(\mathscr{C},\mathscr{D})\frac{AC}{(A-C)(A-D)}$	$+(\mathscr{A},\mathscr{D})\frac{A}{A-D}$			
$1-e^{-Bt}$	$-(\mathscr{A},\mathscr{B})(\mathscr{B},\mathscr{C})(\mathscr{C},\mathscr{D})\frac{ABC}{(A-B)(B-C)(B-D)}$	$+(\mathscr{A},\mathscr{B})(\mathscr{B},\mathscr{D})\frac{AB}{(A-B)(B-D)}$			$-(\mathscr{B},\mathscr{C})(\mathscr{C},\mathscr{D})\frac{BC}{(B-C)(B-D)}+(\mathscr{B},\mathscr{D})\frac{B}{B-D}$		
$1-e^{-Ct}$	$+(\mathscr{A},\mathscr{B})(\mathscr{B},\mathscr{C})(\mathscr{C},\mathscr{D})\frac{ABC}{(A-C)(B-C)(C-D)}$		$+(\mathscr{A},\mathscr{C})(\mathscr{C},\mathscr{D})\frac{AC}{(A-C)(C-D)}$		$+(\mathscr{B},\mathscr{C})(\mathscr{C},\mathscr{D})\frac{BC}{(B-C)(C-D)}$	$+(\mathscr{C},\mathscr{D})\frac{C}{C-D}$	
$1-e^{-Dt}$	$-(\mathscr{A},\mathscr{B})(\mathscr{B},\mathscr{C})(\mathscr{C},\mathscr{D})\frac{ABC}{(A-D)(B-D)(C-D)}$	$-(\mathscr{A},\mathscr{B})(\mathscr{B},\mathscr{D})\frac{AB}{(A-D)(B-D)}$	$-(\mathscr{A},\mathscr{C})(\mathscr{C},\mathscr{D})\frac{AC}{(A-D)(C-D)}$	$-(\mathscr{A},\mathscr{D})\frac{A}{A-D}$	$-(\mathscr{B},\mathscr{C})(\mathscr{C},\mathscr{D})\frac{BC}{(B-D)(C-D)}-(\mathscr{B},\mathscr{D})\frac{B}{B-D}-(\mathscr{C},\mathscr{D})\frac{C}{C-D}$		-1
1							1

FORMULA FOR d SPECIALIZED AS DESCRIBED IN APPENDIX II

	a_0			b_0	c_0	d_0
$1-e^{-At}$	$+(\mathscr{A},\mathscr{B})(\mathscr{B},\mathscr{C})(\mathscr{C},\mathscr{D})\frac{BC}{(A-B)(A-C)}$	$-(\mathscr{A},\mathscr{B})(\mathscr{B},\mathscr{D})\frac{B}{A-B}$	$-(\mathscr{A},\mathscr{C})(\mathscr{C},\mathscr{D})\frac{C}{A-C}+(\mathscr{A},\mathscr{D})$			
$1-e^{-Bt}$	$-(\mathscr{A},\mathscr{B})(\mathscr{B},\mathscr{C})(\mathscr{C},\mathscr{D})\frac{AC}{(A-B)(B-C)}$	$+(\mathscr{A},\mathscr{B})(\mathscr{B},\mathscr{D})\frac{A}{A-B}$		$-(\mathscr{B},\mathscr{C})(\mathscr{C},\mathscr{D})\frac{C}{B-C}+(\mathscr{B},\mathscr{D})$		
$1-e^{-Ct}$	$+(\mathscr{A},\mathscr{B})(\mathscr{B},\mathscr{C})(\mathscr{C},\mathscr{D})\frac{AB}{(A-C)(B-C)}$	$+(\mathscr{A},\mathscr{C})(\mathscr{C},\mathscr{D})\frac{A}{A-C}$	$+(\mathscr{B},\mathscr{C})(\mathscr{C},\mathscr{D})\frac{B}{B-C}$		$+(\mathscr{C},\mathscr{D})$	
1						1

TABLE II

		a_0
	$1-e^{-At}$	$-(\mathscr{A}\mathscr{B})(\mathscr{B}\mathscr{C})\frac{AB}{(A-B)\ (A-C)}+(\mathscr{A}\mathscr{C})\frac{A}{A-C}$
c	$1-e^{-Bt}$	$+(\mathscr{A}\mathscr{B})(\mathscr{B}\mathscr{C})\frac{AB}{(A-B)\ (B-C)}$
	$1-e^{-Ct}$	$-(\mathscr{A}\mathscr{B})(\mathscr{B}\mathscr{C})\frac{AB}{(A-C)\ (B-C)}-(\mathscr{A}\mathscr{C})\frac{A}{A-C}$
	1	

Again, if it were assumed that, of the portion of $\mathscr{A}$ which reacts, a fraction p follows the path $\mathscr{A}\rightarrow\mathscr{B}$ and the fraction $1-p$ follows the path $\mathscr{A}\rightarrow\mathscr{C}$ the system is specified by

$$(\mathscr{A}\mathscr{B}) = (\beta/\alpha)p, \quad (\mathscr{A}\mathscr{C}) = (1-p), \quad (\mathscr{A}\mathscr{D}) = p[1-(\beta/\alpha)];$$
$$(\mathscr{B}\mathscr{C}) = \gamma/\beta, \quad (\mathscr{B}\mathscr{D}) = 1-\gamma/\beta;$$
$$(\mathscr{C}\mathscr{D}) = 1.$$

APPENDIX I

The complete formula for d is given here to display the full pattern of the solutions to the general system. d is determined by the differential equation

$$-dd/dt = Dd-(\mathscr{A}\mathscr{D})Aa-(\mathscr{B}\mathscr{D})Bb-(\mathscr{C}\mathscr{D})Cc,$$

where a, b, c are given by Equations (1), (2), (3) of System II.

APPENDIX II

The general formula for d is here specialized to describe the case in which $\mathscr{D}$ is the final substance in the sequence. That is, $\mathscr{D}$ does not break down ($D = 0$) and all the other substances break down, by all possible routes, into $\mathscr{D}$ and nothing else. It follows that

$$(\mathscr{C}\mathscr{D}) = 1, \quad (\mathscr{B}\mathscr{C})+(\mathscr{B}\mathscr{D}) = 1, \quad (\mathscr{A}\mathscr{B})+(\mathscr{A}\mathscr{C})+(\mathscr{A}\mathscr{D}) = 1.$$

The solution corresponding to these conditions is obtained from the general formula given in Appendix I simply by substituting $D = 0$. The form of the solution is altered somewhat by this substitution, because the argument $1-e^{-Dt}$ vanishes and therefore the corresponding row of multipliers is dropped. The resulting formula for d has the property that the sum of the coefficients in each cell is unity. This corresponds to the fact that, when t becomes infinite,

$$d = a_0+b_0+c_0+d_0 = 1.$$

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NOTES

THE INFRARED AND RAMAN SPECTRA OF ALLENE-1,1-d_2 [1]

By J. C. Evans,[2] J. K. Wilmshurst,[3] and H. J. Bernstein

The infrared spectrum of allene-1,1-d_2 vapor has been observed from 2 to 35 μ (Fig. 1) using a Perkin Elmer Model 12C double pass spectrometer equipped with LiF, NaCl, and CsBr optics and the Raman spectrum obtained for the liquid at −50° C. (Fig. 2) with a White grating Raman spectrometer (8) with photoelectric recording. The depolarization ratios of the Raman lines were obtained by the method of Edsall and Wilson (3).

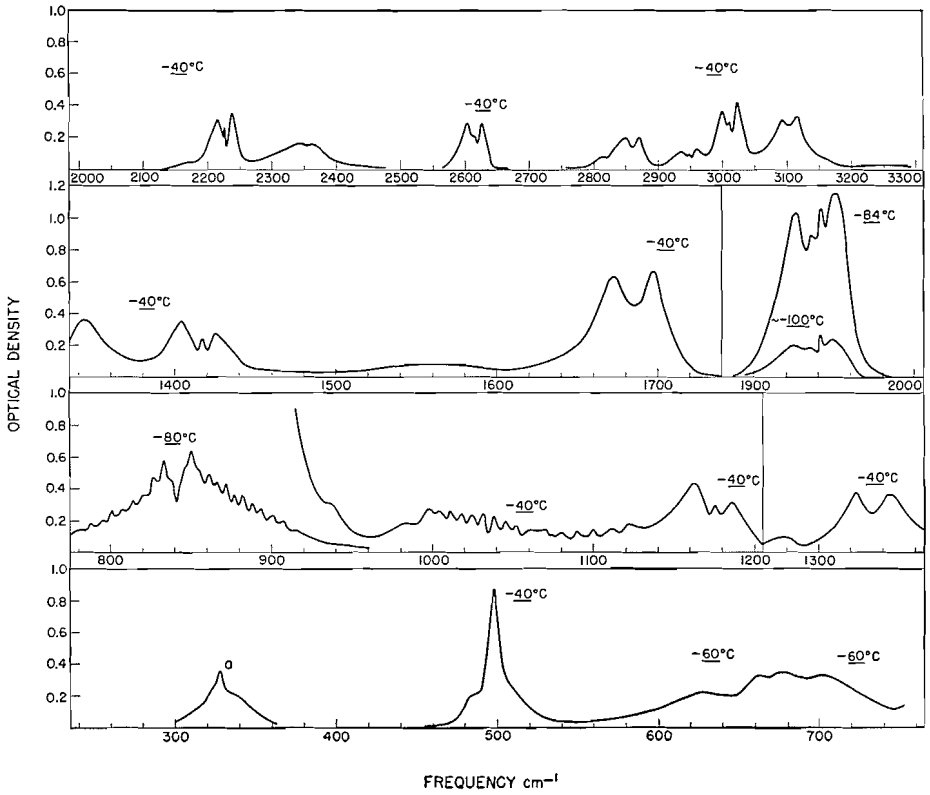

FIG. 1. The infrared spectrum of $H_2C{=}C{=}CD_2$ vapor in a 10 cm. cell at the vapor pressure of the liquid for the temperature shown; (*a*) 6 cm. cell, liquid at −50°C.

[1]*Issued as N.R.C. No. 4011.*
[2]*National Research Laboratories Postdoctorate Fellow 1953–1955.*
[3]*National Research Laboratories Postdoctorate Fellow 1955– .*

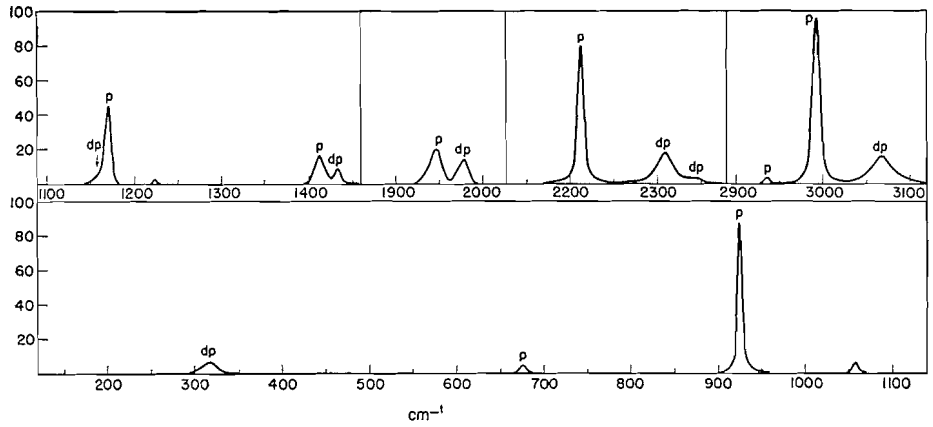

FIG. 2. The Raman spectrum of liquid $H_2C{=}C{=}CD_2$ (slits ~7 cm.$^{-1}$). The intensity of the band at ~3000 cm.$^{-1}$ is taken as 100. dp = depolarized, p = polarized.

TABLE I

FREQUENCY ASSIGNMENT FOR ALLENE-1,1-d_2

V_d	C_{2v}		Approximate description	$CH_2{=}C{=}CH_2$	$CH_2{=}C{=}CD_2$	$CD_2{=}C{=}CD_2$
a_1	a_1	ν_1	C—H stretching	2996	2995 R	2195
a_1	a_1	ν_2	CH_2 bending	1440	1169 R	1228
a_1	a_1	ν_3	C=C=C stretching	1076	924 R	874
b_2	a_1	ν_5	C—H stretching	3005	2226 IR	2230
b_2	a_1	ν_6	C=C=C stretching	1957	1941 IR	1921
b_2	a_1	ν_7	CH_2 bending	1398	1416 IR	1034
b_1	a_2	ν_4	Torsion	865	(750)	615
e	b_1,b_2	ν_8	C—H stretching	3085	3105 IR, 2309 R	2330
e	b_1,b_2	ν_9	CH_2 rocking	1015	1058 R, 842 IR	830
e	b_1,b_2	ν_{10}	CH_2 rocking	842	676 R, 842 IR	667
e	b_1,b_2	ν_{11}	C=C=C bending	354	317 R, 317 R	306

R = *Raman band.*
IR = *infrared band.*
(750) = *calculated from the Teller Redlich product rule (5).*

An assignment of all the fundamentals for allene-1,1-d_2 has been made on the basis of C_{2v} symmetry and this assignment is given in Table I together with that of Lord and Venkateswarlu (6) for allene and allene-d_4.

The type a_1 vibrations in allene-1,1-d_2, corresponding to the a_1 and b_2 type vibrations in allene, give rise to polarized Raman bands and parallel type infrared bands and can be assigned immediately. The type b_1 and b_2 vibrations, corresponding to the type *e* doubly degenerate vibrations of allene, should give rise to depolarized Raman bands and perpendicular type infrared bands and are assigned by comparison with allene and allene-d_4. A partial resolution of the two perpendicular bands at 842 and 1058 cm.$^{-1}$ was obtained. The a_2 torsional frequency was not observed but was computed from the Teller Redlich product rule (5). All the remaining observed frequencies can be easily

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assigned, in terms of these fundamentals, to overtone or combination bands (Table II). The Raman band at 1223 cm.$^{-1}$ is probably ν_1 (2995 cm.$^{-1}$) excited by the 4047 Å mercury line.

The Teller Redlich product rule (5), Decius–Wilson sum rule (2), and Bernstein–Pullin sum rule (1) are consistent with the present assignment (Table III).

On attempting a direct comparison of the a_1 and b_2 frequencies in allene with the a_1 frequencies in allene-1,1-d_2, it is found that an interesting change has

TABLE II

OVERTONE AND COMBINATION BANDS FOR ALLENE-1,1-d_2

Obs. frequency	Assignment	Calc.
498* IR	$\nu_9(b_2)-\nu_{11}(b_2)$	525
626 IR	$2\nu_{11}$	634
1158 R	$\nu_9(b_2)+\nu_{11}(b_1)$	1159
~1285 IR	$\nu_8(b_2)-$[1008]	1301
1334 IR	$2\times\nu_{10}$	1352
1433 R	$\nu_{10}(b_1)+\nu_4(a_2)$	1426
~1566 IR	$\nu_4(a_2)+\nu_9(b_2)$	1592
1686 IR	$2\times\nu_9(b_2)$	1684
1935 IR	$\nu_6(a_1)+\nu_{11}-\nu_{11}$†	1941
1977 R	?	
2173 IR	2×[1086]	2172
2615 IR	$\nu_8(b_2)+\nu_{11}(b_2)$	2626
2812 IR	$2\times\nu_7(a_1)$	2832
2860 IR	$2\times$[1086]$+\nu_{10}(b_1)$	2848
2949 IR	$\nu_6(a_1)+$[1008]	2949

[1086] and [1008] are the estimated positions of the unperturbed fundamentals $\nu_2(a_1)$ and $\nu_3(a_1)$.

**May be due to $CH_3C{\equiv}CD$ impurity which has its strongest infrared band at 498 cm.$^{-1}$ (4).*

†*Consistent with corresponding assignments in allene and allene-d_4 (6).*

TABLE III

PRODUCT RULE RATIOS

		Symmetry species used for ratio calculation		
Theor.	Obs.	CH_2CCH_2	CH_2CCD_2	CD_2CCD_2
0.513	0.519	a_1, b_2	a_1	
0.512	0.527		a_1	a_1, b_2
0.866	—	b_1	a_2	
0.816	—		a_2	b_1
0.382	0.426	e	b_1, b_2	
0.461	0.457		b_1, b_2	e

APPLICATION OF SUM RULES TO ALLENE-1,1-d_2

	$\Sigma\nu^2$, cm.$^{-2}$		$\Sigma\nu$, cm.$^{-1}$	
Species	Theor.	Obs.	Calc.	Obs.
a_1	2.192×10^7	2.192×10^7	10,677	10,671
b_1, b_2	1.792×10^7	1.817×10^7	9,415	9,466

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occurred and two bands in the 1000–1400 cm.$^{-1}$ region, one due to the symmetrical CH_2 bending and the other due to the symmetrical C=C=C stretching frequency, have undergone major changes upon deuterium substitution. This change is explained by the coupling of the symmetrical CD_2 bending mode with the symmetrical C=C=C stretching mode, which give rise to frequencies in the 1000–1100 cm.$^{-1}$ region, causing one frequency to increase to 1169 cm.$^{-1}$, and the other to drop to 924 cm.$^{-1}$. This coupling is also present in allene-d_4, but to a slightly greater extent, the two resultant frequencies being at 1228 cm.$^{-1}$ and 874 cm.$^{-1}$.

The sample of allene-1,1-d_2 was prepared for us through the courtesy of Morse and Leitch (7).

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A NOTE ON THE SYSTEM WOLFRAM–TELLURIUM

By Osvald Knop and Haakon Haraldsen

Goldschmidt (2) considered wolfram ditelluride to be isostructural with wolfram disulphide and wolfram diselenide, but this has never been confirmed by a structural investigation. In fact, in a preliminary study of the binary systems of wolfram with sulphur, selenium, and tellurium, Stangebye (7) showed that the compound WTe_2, prepared by heating stoichiometric amounts of the elements *in vacuo*, did not give X-ray powder diffraction photographs similar to those of the disulphide and diselenide.

This observation was fully confirmed in the present investigation. The rotation and Weissenberg photographs of a single crystal found in the mass of fine ditelluride powder showed that the compound had an orthorhombic structure with the unit-cell dimensions $a = 3.490 \pm 0.006$ Å, $b = 6.277 \pm 0.015$ Å, and $c = 14.07 \pm 0.02$ Å. The volume of the unit cell based on these dimensions, 308 ± 2 Å^3, and the experimental density, $d_4^{20} = 9.40$, led to four WTe_2 units per unit cell. Reflections of the type $(h0l)$ were absent when $h+l = 2n+1$. The space groups consistent with these systematic absences are $D_{2h}^{13} - Pmnm$, $C_{2v}^{7} - Pmn$, and $D_2^3 - P2_122_1$.

Unless WTe_2 is polymorphic—and we obtained no evidence to that effect—it cannot be considered isostructural with the $C7$-type compounds, i.e., with MoS_2, $MoSe_2$, WS_2, and WSe_2. There are indications, however, that it has a

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layer-like structure closely related to the *C*7 type. The axial ratio of WTe_2, $c/a = 4.03$, does not differ greatly from the values 3.92–3.93 and 3.94 for the corresponding sulphur and selenium compounds (9, 10), and a value for b about 3.7% lower than the above value would give an axial ratio $b/a = \sqrt{3}$ required for an orthohexagonal cell. This suggests a modified double unit cell of the *C*7 type. A Patterson projection on the (010) plane seemed to confirm this similarity but the intensity data on which it was based were rather inaccurate. The single crystal used was a very thin plate of irregular shape, with the approximate dimensions 0.15, 0.08, and 0.02 mm. along the *a*-, *b*-, and *c*-axes, respectively, and there must have been heavy irregular absorption of X-rays in the crystal. Powder photographs taken both with an ordinary and with a microfocus camera contained too many diffuse and overlapping lines to permit an intensity evaluation. Attempts are being made to secure more suitable single crystals of WTe_2 that will provide reliable data for a structure determination.

No line shift outside the usual measurement spread was detected in the powder photographs of samples having the gross compositions $WTe_{1.90}$ and WTe_3. These samples were prepared in the same manner as WTe_2 and were annealed *in vacuo* at 500°C. for several days. It seems likely that the homogeneity range of wolfram ditelluride is very narrow (compare the slight variation in the lattice constants reported for WS_2 (9)). This indicates that if the composition of the single crystal used deviated at all from the stoichiometric composition, it could have been only by a very small amount.

In agreement with the results of Stangebye (7) and Morette (4, 5) no compound other than WTe_2 was detected in alloys obtained by direct synthesis *in*

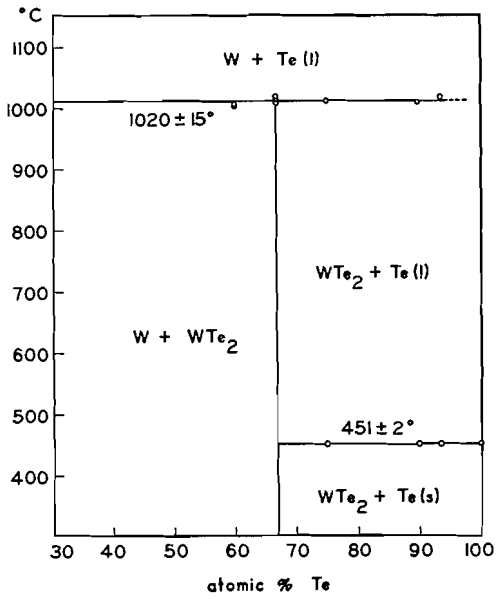

FIG. 1. Phase relationships in the system wolfram–tellurium under orthobaric conditions.

vacuo. Combined evidence from X-ray powder photography, and from thermal analysis of samples sealed in small evacuated quartz containers, suggests phase relationships as represented in Fig. 1, with the system under its own pressure. However, one cannot exclude the possibility that other compounds might be obtained by low-temperature annealing of intimate mixtures of WTe_2 and tellurium or wolfram for long periods of time. As is evident from Morette's examination of polished sections of alloys rich in tellurium (5), the solubility of wolfram in tellurium at temperatures below 500°C. must be quite low, as a solidified alloy with 0.33 at. % W still contained crystals of the ditelluride embedded in a matrix of tellurium.

A fuller account of the continued investigation, and of a similar investigation in the system molybdenum–tellurium now in progress, will be published later.

EXPERIMENTAL

The wolfram used in this investigation was prepared by reducing calcined WO_3 (c.p. grade) with hydrogen at temperatures between 650° and 800°C. The lattice constant of the resulting lightly-sintered powder was found to be 3.1647 ± 0.0003 Å at room temperature, in very good agreement with the value 3.16477 ± 0.00008 Å reported by Cohen (1). Both reduced metal and a commercial wolfram powder reported to contain 99.8% W and 0.2% Mo were used in the preparation of samples with the composition $WTe_{2.00}$. No differences in the properties of the resulting powders were observed.

A grant of tellurium of about 99.9% purity was kindly made by the Research and Development Department of the Canadian Copper Refiners, Limited, Montreal. According to the analysis supplied the main impurity was selenium. The lattice constants of the material were determined as 4.456 ± 0.002 Å and 5.925 ± 0.002 Å, in satisfactory agreement with the values of Straumanis (8), 4.45591 ± 0.00012 Å and 5.92687 ± 0.00002 Å.

Accurately weighed amounts of the elements totalling 15–20 gm. were introduced into degassed clear-quartz tubes which were then evacuated to 10^{-6} mm. Hg, sealed off, and put into a deep vertical tubular furnace at 700–800°C. After several hours the power was turned off and the samples allowed to cool in the furnace. The alloys were then crushed and ground to 100 mesh, thoroughly mixed, and annealed at 500°C. for several days in sealed evacuated quartz tubes. Samples of the gross compositions $WTe_{1.50}$, $WTe_{1.90}$, $WTe_{2.00}$, WTe_3, WTe_4, WTe_9, and WTe_{15} were prepared.

The density of the ditelluride was determined pycnometrically with water as displacement liquid, about 1 cm.^{3} of powder being used in separate determinations. The average of several determinations gave $d_4^{20} = 9.40$. Morette (4, 5) reported $d_4^{15} = 9.44 \pm 0.02$, without mentioning details of his method, while the value calculated from the above lattice constants is 9.46 ± 0.06 gm./cm.^{3}

Although there was practically no loss of material during the handling of the powders, all samples were analyzed. The determination of tellurium using sulphur dioxide and hydrazine hydrate (3) gave satisfactory results. Wolfram was determined as WO_3. The analytical results were in close agreement with

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the intended gross compositions. Indeed, any discrepancies between the analytical results and the compositions of the samples as obtained by weighing are likely to have originated in the inaccuracies inherent in the analytical method.

The samples for thermal analysis were sealed in evacuated containers of clear quartz having internal free volumes of about 3 cm.^{3} An average of about 5 gm. of sample was used in individual runs. There was a pronounced tendency to supercooling, and the geometry of the heating curves depended considerably on the heating rates.

Filtered or unfiltered CuK-radiation ($\lambda\alpha_1 = 1.53740$ kX, $\lambda\alpha_2 = 1.54123$ kX) from a hot-cathode tube was used throughout. The powder photographs were taken in a Straumanis-type camera with a nominal diameter of 114.6 mm., and the rotation and equi-inclination Weissenberg photographs of the single crystal about the a- and b-axes (three and four zones, respectively) were taken in a Unicam instrument, using the multiple-film technique. The intensities were estimated visually. Nelson and Riley's method (6) was used in the treatment of the lattice constants. Difficulties were encountered in the measurement of the films, as WTe_2 did not give good powder photographs.

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This work was begun by the first author in 1948 during his stay at the Institute of Inorganic Chemistry of the University of Oslo, as a part of the studies of the chalkogenides of the transition elements pursued at the Institute for a number of years. A grant from the Norwegian Unesco Committee which enabled him to stay at the Institute is hereby gratefully acknowledged. The investigation was continued at the Nova Scotia Technical College, with financial assistance from the Nova Scotia Research Foundation. The authors wish to express their gratitude to Professor G. V. Douglas for the use of his X-ray diffraction unit; to Dr. D. R. Ryan for the analytical work; to Miss Patricia M. Beatty for assistance with the computations; and to Dr. C. M. Mitchell for a powder photograph of the ditelluride taken with a microfocus unit.

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THE CONDENSATION OF FURAN AND SYLVAN WITH SOME CARBONYL COMPOUNDS[1]

BY W. H. BROWN[2] AND H. SAWATZKY[3]

ABSTRACT

Furan and sylvan condense with aldehydes, chlorinated aldehydes and ketones, and keto acids, in the presence of hydrochloric acid. In most cases, the corresponding difurylalkane or difuryl-substituted acid is formed. In special cases the reaction stops at the furylcarbinol stage.

Difurylalkanes have been accessible, in the past, only through a variety of indirect approaches. Thus, for example, difurylmethane (V) has been prepared by Reichstein, Grussner, and Zschokke (7) by the reduction of difuryl ketone. Gilman and Wright (5) synthesized the same substance by the interaction of 2-chloromercurifuran and furfuryl chloride. Dinelli and Marini (3) treated ethyl furoate with trioxane in the presence of sulphuric acid. By subsequent saponification, hydrolysis, and decarboxylation they obtained difurylmethane. This compound has also been isolated as a product during the acid-catalyzed resinification of furfuryl alcohol (4, p. 222).

Recently, Ackman, Brown, and Wright (1) have reported the formation of 2,2-difurylpropane by the condensation of furan with acetone in the presence of hydrochloric acid. Other methyl ketones gave analogous products.

In the present investigation, it has been found that furan also condenses with aldehydes, chlorinated aldehydes and ketones, and keto acids. The condensation products are difurylalkanes in the case of aldehydes and ketones. With keto acids, the corresponding difuryl-substituted acids result. Chlorinated aldehydes and ketones, when condensed with furan, yield chlorinated difurylalkanes in some cases, while in others, unstable products, thought to be chlorinated furylcarbinols, are formed. Willard and Hamilton (8) have already reported the condensation of furan (I) with chloral (VIII) to form 1-furyl-2,2,2-trichloroethanol (IX).

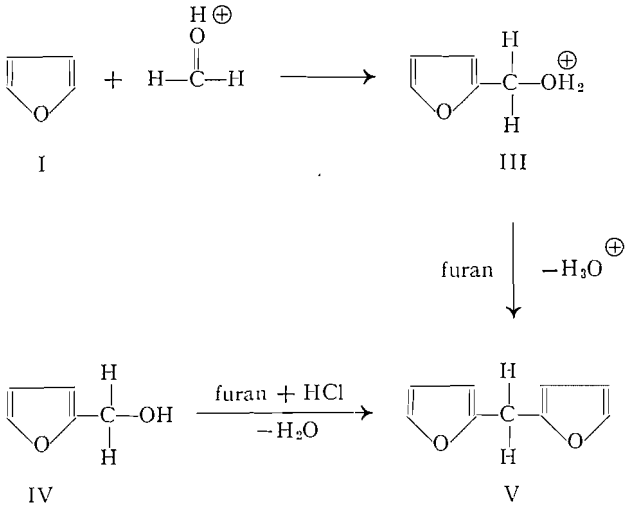
The investigation also includes the reaction of sylvan (2-methylfuran) (II) with the carbonyl compounds previously cited. Analogous products are obtained.

[1]*Manuscript received in original form December 30, 1955, and, as revised, May 25, 1956. Contribution from the Department of Chemistry, Ontario Agricultural College, Guelph, Ontario.*
[2]*Associate Professor of Chemistry, Ontario Agricultural College, Guelph, Ontario.*
[3]*Present address: Department of Chemistry, Wallberg Building, University of Toronto, Toronto, Ontario.*

Tables I, II, and III show the specific carbonyl compounds concerned and data on the products formed.

When furan (I) is treated with aqueous formaldehyde solution in the presence of hydrochloric acid, difurylmethane (V) is formed in low (1.7%) yield. The identity of the product was established by mercuration according to the method of Gilman and Wright (5). A mixture melting point of this mercurial with the mercurial of difurylmethane, the latter prepared by the procedure of Dinelli and Marini (3), showed no depression.

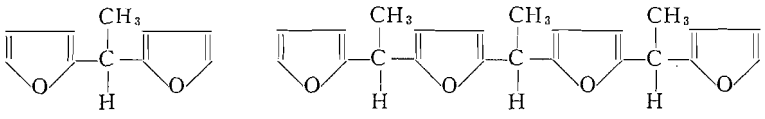
The proposed mechanism for the reaction is as follows:



I III IV V

It seems likely that protonated furfuryl alcohol (III) is an intermediate in the reaction, since furfuryl alcohol (IV), when treated with furan in the presence of hydrochloric acid, forms difurylmethane (V) in increased (15%) yield. No apparent reaction occurs between furfuryl alcohol and furan in the absence of acid. Other acidic compounds might also serve as catalysts (8).

In the reaction of acetaldehyde with furan, two products, 1,1-difurylethane (VI) and 1,1-*bis*[5-(methylfurfuryl)-furyl]ethane (VII), can be isolated.



VI VII

Here, again, the protonated furylcarbinol appears to be the intermediate, since 1,1-difurylethane (VI) is formed when methyl-furylcarbinol is treated with furan in the presence of hydrochloric acid.

Inspection of Table I shows that the yields of 1,1-disubstituted alkanes are

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TABLE I

CONDENSATION PRODUCTS OF ALDEHYDES WITH FURAN AND SYLVAN

Reactants	Yield, %	B.p., ° C./mm.	$n_D^{t°}$	$d_{4°}^{20°}$	Molecular formula	Analysis	
						Calc.	Found
Furan and:							
Formaldehyde	1.7	79–81/12	1.4991/16	1.098	$C_9H_8O_2$		
Acetaldehyde	58	86–87/15	1.4993/20	1.073	$C_{10}H_{10}O_2$	C, 74.1; H, 6.21	C, 74.0; H, 6.05
	9.7	136–137/4	1.5218/20	1.105	$C_{22}H_{22}O_4$	C, 75.4; H, 6.33	C, 75.3; H, 6.44
Propionaldehyde	24	88–93/15	1.4930/20	1.047	$C_{11}H_{12}O_2$	C, 75.0; H, 6.87	C, 75.2; H, 7.33
Butyraldehyde	38	108/14	1.4890/20	1.015	$C_{12}H_{14}O_2$	C, 75.8; H, 7.42	C, 76.1; H, 7.58
Benzaldehyde	No reaction						
Furfural	No reaction						
Glyoxal	No reaction						
Sylvan and:							
Formaldehyde	34	114/15	1.5017/20	1.042	$C_{11}H_{12}O_2$	C, 75.0; H, 6.87	C, 75.6; H, 6.88
Acetaldehyde	61	113/12	1.4993/20	1.027	$C_{12}H_{14}O_2$	C, 75.7; H, 7.42	C, 75.8; H, 7.42
Propionaldehyde	63	118/14	1.4949/20	1.008	$C_{13}H_{16}O_2$	C, 76.4; H, 7.96	C, 76.8; H, 7.87
Butyraldehyde	73	132/15	1.4935/20	0.989	$C_{14}H_{18}O_2$	C, 77.0; H, 8.32	C, 77.0; H, 8.11

higher from sylvan than from furan. This points up the activating influence at the 2-position of an electron-donating group located on the 5-position of the furan nucleus (4, p. 27).

In Table II it may be seen that the presence of halogen in the carbonyl compound reduces the yield of the halogenated difurylalkane. The presence of

TABLE II

CONDENSATION PRODUCTS OF CHLORINATED ALDEHYDES AND KETONES WITH FURAN AND SYLVAN

Reactants	Yield, %	B.p., °C./mm.	$n_D^{20°}$	$d_{4°}^{20°}$	Molecular formula	Analysis	
						Calc.	Found
Furan and:							
Chloroacetaldehyde		Decomposes			$C_6H_7O_2Cl$	Cl, 24.2	Cl, 22.3
Monochloroacetone	19	127–131/15	1.5208	1.170	$C_{11}H_{11}O_2Cl$	Cl, 16.9	Cl, 16.6
1,3-Dichloroacetone		Decomposes					
Sylvan and:							
Chloroacetaldehyde	11	142–144/14	1.5176	1.143	$C_{12}H_{13}O_2Cl$	Cl, 15.8	Cl, 15.7
Dichloroacetaldehyde		Decomposes					
Monochloroacetone	23	138–142/14	1.5160	1.115	$C_{13}H_{15}O_2Cl$	Cl, 14.9	Cl, 14.9
1,3-Dichloroacetone	5.2	175–179/14	1.5308	1.159	$C_{13}H_{14}O_2Cl$	Cl, 26.0	Cl, 26.0

an electron-donating group, such as methyl, either on the furan ring or in the carbonyl compound partially offsets the deactivating effect of chlorine in the carbonyl compound.

As shown by Willard and Hamilton (8), when furan (I) reacts with chloral (VIII) in the presence of zinc chloride and glacial acetic acid, the product is 1-furyl-2,2,2-trichloroethanol (IX) in fair yield. The inductive effect of the halogens decreases the basicity of the oxygen and to some extent increases the C—O bond strength by forcing participation of the unshared

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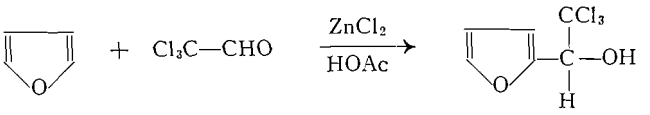
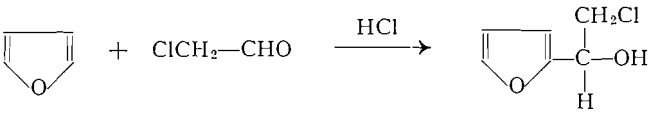
electrons of oxygen in this bonding. Hence the OH becomes less likely to be protonated and thus less labile than in the unsubstituted cases.



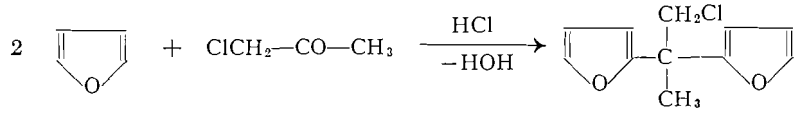
I VIII IX

In the case of some of the halogenated carbonyl compounds, the reaction with furan appears to have stopped at the carbinol stage. Thus, for example, furan (I) reacts with chloroacetaldehyde (X) to yield 1-furyl-2-chloroethanol (XI).



I X XI

However, when furan (I) and monochloroacetone (XII) are treated with hydrochloric acid the product of the reaction is 1-chloro-2,2-difuryl-propane (XIII). Here the methyl group is able to overcome the inhibiting action of the chlorine atom.



I XII XIII

In the reaction of furan and sylvan with keto acids (Table III), some of the products are those which one would expect on the basis of normal reaction.

TABLE III

CONDENSATION PRODUCTS OF KETO ACIDS AND ESTERS WITH FURAN AND SYLVAN

Reactants	M.p., ° C.	B.p., ° C./mm.	Yield, %	Molecular formula	Analysis	
					Calc.	Found
Furan and:						
Levulinic acid	68.5–69.5	180–220/17	29	$C_{13}H_{14}O_4$	N.E., 234	N.E., 232
Pyruvic acid	Gave only resins					
Ethyl acetoacetate		140–170/17	11 wt. %			
Sylvan and:						
Levulinic acid	84–85	207–230/16	33	$C_{15}H_{18}O_4$	C, 68.7; H, 6.91 N.E., 262	C, 69.1; H, 6.76 N.E., 261
Pyruvic acid	110.5–111.5		68	$C_{13}H_{14}O_4$	C, 66.6; H, 6.02 N.E., 234	C, 66.8; H, 6.11 N.E., 231
Acetoacetic acid		135–210/3	36 wt. %			
Ethyl acetoacetate		170–220/16	43 wt. %			

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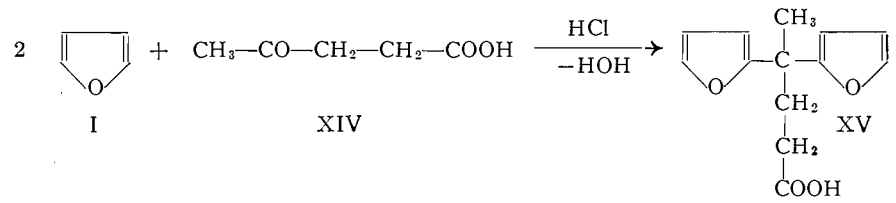
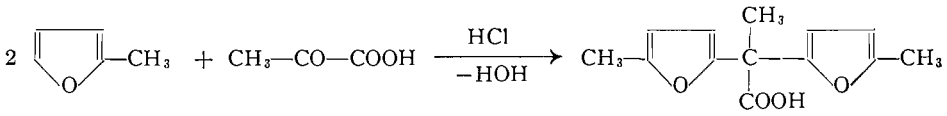
Thus, for example, furan (I) reacts with levulinic acid (XIV) to form γ-*bis*(furyl)-valeric acid (XV).



I XIV XV

While sylvan (II) reacts normally with pyruvic acid (XVI) to form α-*bis*(sylvyl)-propionic acid (XVII), furan reacts violently to yield a resinous product.



II XVI XVII

Both furan and sylvan react vigorously with ethyl acetoacetate in the presence of hydrochloric acid. The product in each case is an oil which does not lend itself readily to purification. These oils have not been investigated further.

Ackman, Brown, and Wright (1) prepared substituted tetroxaquaterenes by condensing difurylalkanes with the parent methyl ketones. In view of this, difurylmethane would be expected to condense with formaldehyde to form the unsubstituted tetroxaquaterene. Attempts to produce such a compound failed.

When 1,1-difurylethane (VI) and 1,1-*bis*[5-(methylfurfuryl)-furyl]ethane (VII) were treated with acetaldehyde in the presence of hydrochloric acid, resinous products were formed. No tetroxaquaterene formation occurred.

EXPERIMENTAL

All melting points have been corrected against reliable standards. Molecular weights were determined by Rast method. For the sake of brevity, only a few of the preparations are reported in operational detail. It may be assumed that the products listed in Tables I, II, and III may be obtained by following the procedure outlined for preparing a homologue.

Difurylmethane (V)

(*a*) *From Furan and Formaldehyde*

Into a 2-liter three-necked round-bottom flask fitted with a stirrer were introduced 50 ml. of 20% hydrochloric acid and 190 ml. (2.5 moles) of 36% aqueous formaldehyde solution. While cooling externally with tap water (14° C.), 170 gm. (2.5 moles) of furan was added dropwise over a period of 30 min. After five hours the reaction mixture was neutralized with solid sodium carbonate and then steam distilled. The distillate was extracted with ether, and the ether solution washed with 28% aqueous ammonia solution to remove

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formaldehyde and then with water to remove ammonia. The ether solution, after being dried over anhydrous magnesium sulphate, was evaporated. The residual oil was distilled under diminished pressure giving 3.10 gm. (1.7%) of a colorless oil, b.p. 79–81° C. (13 mm. Hg); $\eta_D^{16°}$ 1.4991; $d_{4°}^{20°}$ 1.098. Physical constants reported for difurylmethane (4, p. 78) are: b.p. 78° (12 mm. Hg); $\eta_D^{20°}$ 1.5049; $d_{4°}^{20°}$ 1.102.

(*b*) *From Furan and Furfuryl Alcohol*

In a 125 ml. Grignard-type flask, fitted with a stirrer, were placed 17 gm. (0.25 mole) of furan, 24.5 gm. (0.25 mole) of furfuryl alcohol, and 5 ml. of 37% hydrochloric acid. The mixture was cooled to 13° C. and stirred vigorously for four hours at this temperature. When the reaction mixture was worked up according to the procedure outlined in (*a*), 5.65 gm. (15%) of a colorless oil was obtained. This oil had identical physical constants with the oil described in (*a*).

Both oils were shown to be identical by mixture melting point of their mercurials, m.p. 149.5°, prepared by the method of Gilman and Wright (5). A mixture melting point of these mercurials with the mercurial of difurylmethane, m.p. 149.5°, the latter prepared by the procedure of Dinelli and Marini (3), showed no depression.

1,1-Difurylethane (VI)

(*a*) *From Furan and Methyl-furylcarbinol*

To 0.2 mole of methyl-furylcarbinol Grignard complex, prepared *in situ* by the method of Peters and Fischer (6), was added 17 gm. (0.25 mole) of furan. The ice-cold mixture was stirred while 100 ml. of water was added, and the resulting mixture treated with 37% hydrochloric acid until 5 ml. were in excess. After it had been stirred for two and one-half hours the reaction mixture was neutralized with solid sodium carbonate and steam distilled. The oil obtained by this procedure distilled at 84–87° C. (15 mm. Hg), and weighed 7.3 gm. (22%); $\eta_D^{20°}$ 1.5003; $d_{4°}^{20°}$ 1.072.

(*b*) *From Furan and Acetaldehyde*

In a 250 ml. Grignard-type flask, fitted with a stirrer, were placed 20 ml. of 37% hydrochloric acid, 20 ml. of water, and 136 gm. (2.0 mole) of furan. After the flask had been cooled externally with tap water at 15° C., 44 gm. (1.0 mole) of acetaldehyde was added dropwise over a period of 100 min. Stirring at 15° C. was continued for 17 hr. At the end of this time, 200 ml. of water was added to the mixture which was then made alkaline by the addition of saturated sodium bicarbonate solution. After it was extracted with 200 ml. of ether, the ether solution was separated, washed with 100 ml. of water, and dried over anhydrous sodium sulphate. After the ether was flashed off, the residual brown oil was fractionated in a column as described by Bower and Cooke (2). The first fraction was a colorless oil weighing 94.5 gm. (58%) and boiling at 86–87° C. (15 mm. Hg); $\eta_D^{20°}$ 1.4993; $d_{4°}^{20°}$ 1.073. Anal. Calc. for $C_{10}H_{10}O_2$ (162.18): C, 74.1; H, 6.21. Found: C, 74.0; H, 6.05.

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It is important that the order of addition of reagents to the flask be as indicated. If the acetaldehyde is mixed with the acid, and furan added subsequently, paraldehyde is the chief product.

1,1-bis[5-(Methylfurfuryl)-furyl]ethane (VII)

A second fraction from the preceding distillation, a pale yellow oil, boiled at 136–137° C. (3–4 mm. Hg). It weighed 11.3 gm. (9.7%); $\eta_D^{20°}$ 1.5218; $d_{4°}^{20°}$ 1.105. Anal. Calc. for $C_{22}H_{22}O_4$: C, 75.4; H, 6.33; mol. wt., 350. Found: C, 75.3; H, 6.44; mol. wt., 330.

1-Chloro-2,2-difurylpropane (*XIII*)

In a 250 ml. Grignard-type flask, fitted with a stirrer, were placed 34 gm. (0.5 mole) of furan, 23 gm. (0.25 mole) of monochloroacetone, and 10 ml. of 20% hydrochloric acid. The mixture was stirred for 55 hr. at 20° C. A greenish viscous mass formed. After it was neutralized with solid sodium carbonate the mixture was steam-distilled. The colorless oil obtained in this manner distilled at 127–128° C. (15 mm. Hg). It weighed 10.0 gm. (19%) and had $\eta_D^{20°}$ 1.5208; $d_{4°}^{20°}$ 1.170. Anal. Calc. for $C_{11}H_{11}O_2Cl$ (210.60): Cl, 16.9. Found: Cl, 16.6.

α-bis(Sylvyl)-propionic acid (*XVII*)

In a 250 ml. Grignard-type flask, fitted with a stirrer, were placed 22 gm. (0.25 mole) of pyruvic acid, 41 gm. (0.50 mole) of sylvan, and 5 ml. of 37% hydrochloric acid. The mixture evolved heat and was cooled to 11° C. while stirring for two hours, at which time it was partially neutralized with sodium carbonate. A solid weighing 40 gm. (68%) formed.

The acid was difficult to purify, but repeated crystallization from acetone–hexane gave light brown cubes, m.p. 110.5–111.5° C. Anal. Calc. for $C_{13}H_{14}O_4$: C, 66.6; H, 6.02; N.E., 234. Found: C, 66.8; H, 6.11; N.E., 231.

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We are indebted to the du Pont Company of Canada for generous supplies of furan and to Mr. G. Bedrosian for technical assistance.

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THE OXIDATION OF HYDRAZOBENZENE BY AMMONIUM PERSULPHATE IN ACETONITRILE–WATER SOLUTION[1]

By B. J. P. Whalley, H. G. V. Evans, and C. A. Winkler

ABSTRACT

In a given experiment, second order kinetics were displayed during the greater part of the reaction over a considerable range of initial concentrations of reactants. In general, the second order behavior was maintained to greater extent of reaction when hydrazobenzene was in excess. The calculated second order rate constant, k, decreased with increase in initial hydrazobenzene concentration and increased with increase in initial concentration of ammonium persulphate. For different equimolar concentrations of reactants, k was virtually independent of initial concentrations. The value of k was proportional to the square root of the ratio of the initial concentrations of persulphate and hydrazobenzene. The activation energy of the over-all reaction was 16 kcal. per mole. A free radical mechanism appears to account reasonably well for the major experimental observations.

INTRODUCTION

The oxidation of mercaptans by potassium persulphate in glacial acetic acid – water solution has been discussed in a previous paper from this laboratory (3). In respect of persulphate disappearance, the reaction was found to change from first to second order as the mercaptan concentration was reduced to a sufficiently low value. The calculated first order constant decreased with increase of persulphate concentration, but was independent of the chain length of the aliphatic mercaptan used. A secondary salt effect was observed; sulphate ions and sulphuric acid increased the rate, while potassium ions retarded it. An activation energy of 26,000 cal. per mole was found for the reaction. The experimental data were explained by a mechanism involving the attack on mercaptan by sulphate ion radicals formed by thermal decomposition of persulphate ions. Although Levitt (6) has recently suggested that the data could be more satisfactorily interpreted if sulphur tetroxide rather than the sulphate ion radical were considered the reactive entity, Eager and McCallum (2) have shown by radioactive evidence that such a mechanism is untenable.

Bartlett and Nozacki (1) have found that the addition of methanol to a buffered aqueous solution of persulphate largely increased the rate of persulphate decomposition. The rate was found to be three-halves order in persulphate and half order in methanol. The results appear to be satisfactorily explained by a free radical mechanism, in which the initial formation of sulphate ion radicals resulted from the direct reaction of persulphate with methanol rather than unimolecular decomposition of persulphate. Bartlett's mechanism has been challenged by Kolthoff *et al.* (5) since the addition of allyl acetate virtually eliminates the rapid disappearance of persulphate in the presence of methanol.

[1]*Manuscript received April 23, 1956.*
Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Quebec, with financial assistance from the National Research Council.

The present study was made with a view to obtaining further information about the oxidation of organic molecules by persulphate in homogeneous systems, particularly when the organic reactant is one that might be considered exceedingly susceptible of oxidation. To this end hydrazobenzene was chosen as the substrate.

EXPERIMENTAL AND RESULTS

The glacial acetic acid – water solvent used in the previous study with mercaptans was unsatisfactory for present purposes, owing to the formation of a blue-black coloration, followed by a dark precipitate, when hydrazobenzene was added to the solution of persulphate. A mixed solvent consisting of 100 ml. acetonitrile and 12.5 ml. water was found to be satisfactorily stable under the experimental conditions it was desired to use; at 25° C., the rate of disappearance of ammonium persulphate (0.0015 *M*) in the solvent was negligible, while at 45° C., a rate of only 0.3% per hour was measured when the initial concentration was 0.006 *M*.

Technical grade acetonitrile (Brickman and Co., Montreal) was dried over sodium sulphate and distilled through a Widmer column. The fraction boiling between 82.0° and 82.5° C. was collected. It was found that acetonitrile once distilled in this way gave rate data that were within 5% of values obtained when doubly distilled solvent was used; hence for practically all the experiments the acetonitrile was distilled only once.

Distilled water that had been redistilled through a quartz condenser was used for most of the work, although regular laboratory distilled water from a Barnstead still was found to give equally good results.

Ammonium persulphate, reagent grade, from Brickman and Co., Montreal, was used as received. It was stored in brown bottles in a vacuum desiccator over sulphuric acid.

Hydrazobenzene was obtained from the same company and stored under vacuum. Before use, it was recrystallized from ethanol and washed with ice-cold 50% ethanol–water until the filtrate showed no yellow color. The pure white crystals were immediately transferred to a vacuum desiccator and pumped dry with a high vacuum pump. The melting point of the purified material was invariably sharp at 126.5° C. (uncorr.).

The rate of reaction between hydrazobenzene and persulphate was measured by determining the rate of formation of azobenzene with a Fisher Electrophotometer. Formation and intensification of a yellow color in the solution was shown to be due to azobenzene by comparing the absorption spectrum of a reaction mixture after about 10% reaction with that for azobenzene in acetone, using a Beckman spectrophotometer, model DU. For analytical purposes, the electrophotometer was calibrated against solutions of azobenzene of known concentrations in the acetonitrile–water solvent.

Some experiments were made in which the sulphuric acid formed during reaction was titrated with standard base. This method of following the reaction was only approximate, owing to a difficult end point in the yellow reaction mixture. Phenol red was the only indicator found to be at all satisfactory.

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Attempts to follow the disappearance of persulphate by the volumetric method of Kolthoff *et al.* (4) were unsuccessful, owing to some undetermined effect of hydrazobenzene; differential potentiometric titrations (7) also were unsuccessful.

Preliminary experiments indicated that hydrazobenzene was rapidly oxidized when a solution of it in acetonitrile–water was exposed to air. Hence, experimental conditions were arranged to minimize the amount of oxygen in the solvent and entrained in the solid reactants. Acetonitrile was deoxygenated by refluxing it for half an hour, after which it was cooled and stored under a positive pressure of oxygen-free nitrogen. Distilled water was deoxygenated with a stream of oxygen-free nitrogen and stored under a positive pressure of the gas. By suitable techniques for sweeping with oxygen-free nitrogen it was possible to prevent contamination of the reaction mixture with oxygen while it was being made and while samples were being taken for analysis. Checks were made for oxygen contamination with blank experiments (no persulphate present) under the same conditions and at the same time that each series of experiments with persulphate was in progress. At no time was any correction necessary for oxidation due to oxygen.

In a preliminary experiment with hydrazobenzene in excess over persulphate (0.024 M and 0.0060 M respectively) it was found that when reaction was complete the yield of azobenzene was within 2.5% of the amount that should be formed if one mole of persulphate oxidized one mole of hydrazobenzene. The stoichiometry of the reaction may therefore be represented

$$S_2O_8^{=} + (C_6H_5NH)_2 \rightarrow 2HSO_4^{-} + (C_6H_5N)_2.$$

Experiments were made to determine the order of the reaction and the effect on specific rate of varying the initial reactant concentrations. The data were found to conform best to a second order rate equation, and are presented accordingly.

In Fig. 1 are shown some typical second order plots for different initial concentrations of hydrazobenzene at given (0.0060 M) initial persulphate concentration. The increase in calculated second order rate constant towards the end of reaction was observed in most of the experiments. In general, it appeared that, when either hydrazobenzene or ammonium persulphate concentration was held constant at 0.006 M, and the concentration of the other increased, second order linearity tended to be preserved to larger extents of reaction. This seemed to be particularly true when hydrazobenzene was the reactant in excess. At persulphate concentrations below 0.006 M, second order linearity appeared to exist to larger extents of reaction when hydrazobenzene concentrations were correspondingly low. The dependence of extent of linearity on which of the reactants was in excess was more pronounced at higher than at lower temperatures.

The calculated second order rate constant was dependent upon initial concentration of the reactants in the manner shown in Table I and Fig. 2. Although the results were generally reproducible within about 5% at the higher concentrations, they tended to be more variable as the concentrations

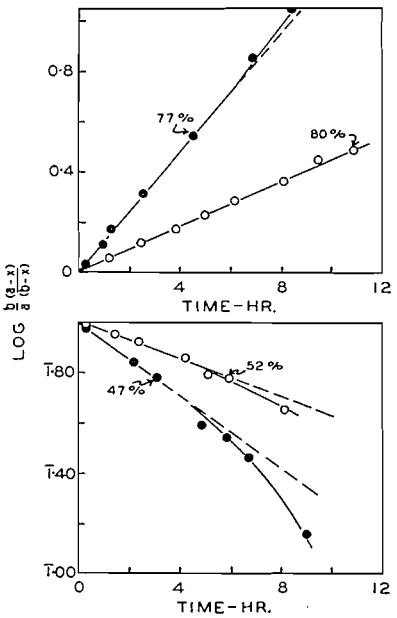

FIG. 1. Typical second order plots.
Temp. 25.02±0.02°C.
Initial concentration ammonium persulphate, 0.00600 mole/liter.
Initial concentration hydrazobenzene:
Upper frame: ●—0.0120 mole/liter.
○—0.0240 mole/liter.
Lower frame: ●—0.00300 mole/liter.
○—0.00150 mole /liter.

TABLE I

EFFECT OF DIFFERENT INITIAL CONCENTRATIONS OF HYDRAZOBENZENE AND AMMONIUM PERSULPHATE ON THE CALCULATED SECOND ORDER RATE CONSTANT

Hydrazobenzene, M./l.	Ammonium persulphate = 0.006 M./l. k (l. m.$^{-1}$ hr.$^{-1}$) 25.02± 0.01°C.	35.28± 0.01°C.	45.75± 0.02°C.	Ammonium persulphate, M./l.	Hydrazobenzene = 0.006 M./l. k (l. m.$^{-1}$ hr.$^{-1}$) 25.02± 0.01°C.	35.28± 0.01°C.	45.75± 0.02°C.
0.00150	40	118		0.00063			59
0.00155	37			0.0015	14	36	
0.0030	24	66	143	0.0030	18	45	101
0.0030	35			0.0060	20	43	115
0.0030	28			0.0060	20	45	118
0.0060	20	43	115	0.012		47	135
0.0060	20	45	118	0.015	22		143
0.012	17	42	91	0.015	21		
0.012	17			0.024		62	
0.018	18			0.030	24		
0.018	16			0.031	25		
0.020	—	39					
0.024	15						
0.030	—	32	79				
0.0395	9						

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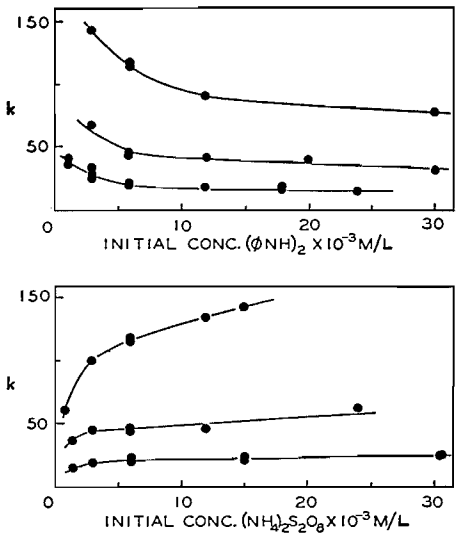

FIG. 2. Dependence of second order rate constant on initial concentration of the reactants.
Upper frame: Initial concentration of ammonium persulphate, 0.00600 mole/liter.
Lower frame: Initial concentration of hydrazobenzene 0.00600 mole/liter.
Temperatures: top curves, 25.02°C.
middle curves, 35.28°C.
bottom curves, 45.75°C.

were reduced. However, there appears to be no doubt that the changes in k represented by Fig. 2 are real.

When experiments were made at 25° C. with equimolar concentrations lower than 0.006 M, the rates were relatively independent of concentration of the reactants, as indicated by the following data:

Initial concn. of hydrazobenzene and ammonium persulphate (M./l.)	k (l. m.$^{-1}$ hr.$^{-1}$)
0.0015	20
0.0030	22
0.0045	20
0.0060	20

Two experiments made at 0° C. with 0.0060 M persulphate gave the following results:

Initial concn. of hydrazobenzene (M./l.)	k (l. m.$^{-1}$ hr.$^{-1}$)
0.0060	1.7
0.036	1.4

These data, together with those of Table I, were used to calculate the activation energy for the reaction at different relative concentrations of the

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two reactants. There appeared to be no significant change of activation energy with initial concentration of reactants, and a value of 16 ± 0.5 kcal. per mole may be assigned to the over-all reaction.

An attempt to determine the effect of added sulphuric acid on the reaction rate was frustrated by the almost immediate formation of a white precipitate in the reaction mixture. A similar precipitate, determined in one experiment by filtration and weighing to amount to about 3% of the hydrazobenzene and 2% of the persulphate taken, was observed in most of the reaction mixtures as reaction approached completion. This precipitate was insoluble in acetonitrile and in water, and did not melt below 300° C. Its identity was not established, since it represented such a small proportion of the reactants consumed.

Three experiments were made in which the increase in titratable acid in the reaction mixture was followed simultaneously with photometric determinations of the azobenzene formed. The initial concentrations of hydrazobenzene and ammonium persulphate were 0.0060 *M* and 0.0060 *M*, 0.0090 *M*, and 0.012 *M* respectively. As indicated earlier, the acidity determinations were rather approximate but all three experiments showed that less titratable acid was formed than would be expected from the amount of hydrazobenzene consumed. The deficit amounted to 15–20%.

DISCUSSION

Although the stoichiometry and the reasonably good second order kinetic behavior of the reaction might be interpreted in terms of a single step oxidation, it seems more probable (8) that at least two single electron transfer steps are involved. In view of this, the following reaction sequence is suggested:

$$S_2O_8^{=} + C_6H_5NHNHC_6H_5 \xrightarrow{k_1} HSO_4^- + C_6H_5NH\dot{N}C_6H_5 + SO_4^{\cdot-}$$

$$SO_4^{\cdot-} + C_6H_5NHNHC_6H_5 \xrightarrow{k_2} HSO_4^- + C_6H_5NH\dot{N}C_6H_5$$

$$S_2O_8^{=} + C_6H_5NH\dot{N}C_6H_5 \xrightarrow{k_3} HSO_4^- + SO_4^{\cdot-} + C_6H_5NNC_6H_5$$

$$2C_6H_5NH\dot{N}C_6H_5 \xrightarrow{k_4} C_6H_5NHNHC_6H_5 + C_6H_5NNC_6H_5$$

The scheme neglects a possible reaction, viz.

$$SO_4^{\cdot-} + C_6H_5NH\dot{N}C_6H_5 \rightarrow HSO_4^- + C_6H_5NNC_6H_5,$$

inclusion of which makes mathematical treatment difficult.

If, for ease of representation, $P = S_2O_8^{=}$, $H = C_6H_5NHNHC_6H_5$, $A = C_6H_5NNC_6H_5$, the usual steady state assumptions give the rate of formation of azobenzene as

$$[1] \qquad \frac{dA}{dt} = k_3[P]\sqrt{\frac{k_1}{k_4}[H][P]} + k_1[H][P]$$

$$[2] \qquad = k_1[H][P]\left(\frac{k_3}{\sqrt{k_1k_4}} \cdot \sqrt{\frac{[P]}{[H]}} + 1\right).$$

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However, because of the apparent second order kinetics of the greater part of most of the reactions, the usual second order rate equation was assumed to be applicable, that is:

$$[3] \qquad \frac{dA}{dt} = k\,[H][P],$$

where k is the calculated second order rate constant recorded in Table I and Fig. 2. Hence,

$$[4] \qquad k = k_1\left(\frac{k_3}{\sqrt{k_1k_4}}\cdot\sqrt{\frac{[P]}{[H]}}+1\right)$$

or

$$k \propto \sqrt{[P]/[H]}\,.$$

Equation [4] predicts, for a reaction scheme of the type postulated, that the calculated second order rate constant, k, should be large for relatively large concentrations of persulphate, small for relatively large concentrations of hydrazobenzene, and independent of concentration for equimolar concentrations of the two reactants. All of these conditions were realized experimentally.

In Fig. 3 are plotted the values of k against $\sqrt{[P]/[H]}$. Extrapolation of

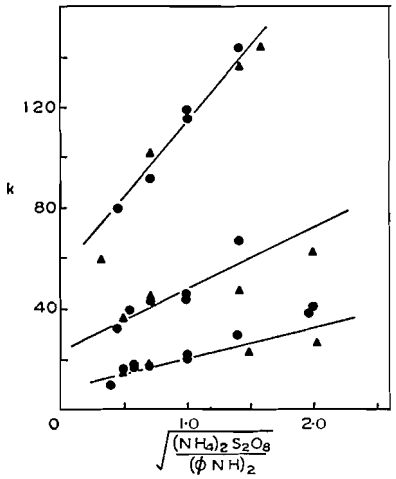

FIG. 3. Plots of second order rate constant against $\sqrt{[\text{Persulphate}]/[\text{Hydrazobenzene}]}$.
●—Initial concentration ammonium persulphate, 0.00600 mole/liter.
▲—Initial concentration hydrazobenzene, 0.00600 mole/liter.
Temperatures for lower, middle, and upper curves were 25.02°, 35.28°, and 45.75°C. respectively.

these lines to zero gave values of k_1, the second order rate constant for the attack of hydrazobenzene by persulphate ion, the chain initiation step, at the three temperatures. The values so obtained were:

T (°K.)	k_1 (l. m.$^{-1}$ hr.$^{-1}$)
298.0	7.5
308.3	23.0
318.8	54.0

These values give a very satisfactory Arrhenius line, corresponding to an activation energy of 17.5 kcal./mole.

It should be mentioned, perhaps, that conductance measurements indicated ammonium persulphate in the acetonitrile–water solvent used to be only weakly ionized. Hence, true persulphate ion concentrations in the reaction mixture would be less than values used in the calculations and plots. The discrepancy would be the less, the higher the temperature. Unfortunately, correction of the persulphate concentration was not possible since, as usual with weakly ionized solutes, curvature of the relation between equivalent conductance and square root of the concentration did not permit evaluation of the conductance at infinite dilution, hence the degree of dissociation.

To determine whether the rate constant k_1 evaluated from individual experiments would be independent of initial concentration of reactants (to replace the concentration dependent k), equation [2] was integrated to yield

$$[5] \qquad k_1 t \frac{([P]-[H])}{2} = \ln \frac{\sqrt{[H]/[P]}+k_5}{\sqrt{([H]-x)/([P]-x)}+k_5}$$

or

$$[6] \qquad k_1 t = \left\{\frac{2}{[P]-[H]} \cdot \ln\left(\sqrt{\frac{[H]}{[P]}}+k_5\right)\right\} - \left\{\frac{2}{[P]-[H]} \cdot \ln\left(\sqrt{\frac{[H]-x}{[P]-x}}+k_5\right)\right\}$$

where $k_5 = k_3/\sqrt{k_1 k_4}$ and k_1 is the rate constant for the initiation step.

Expansion of equation [6] gives

$$[7] \qquad k_1 = \left\{\frac{2}{([P]-[H])t} \cdot \ln \frac{(1-x/[P])}{(1-x/[H])}\right\} + \left\{\frac{2k_5}{([P]-[H])t}\left(\sqrt{\frac{[P]}{[H]}}-\sqrt{\frac{[P]-x}{[H]-x}}\right)\right\} + \cdots = 2k+2k_5A.$$

Values of k and A were calculated for different times in a given experiment at 25.02° C. for various initial concentrations of the reactants, and average values of the two quantities obtained.

From a plot of k against A, a value for k_5 at 25.02° C. of 0.6 was obtained. This value of k_5 was put into Equation [6] and the second term on the right-hand side of this equation was plotted against time for various concentrations of hydrazobenzene and persulphate. From the slopes of these plots, values of k_1 were obtained and these in turn were plotted against initial concentrations of hydrazobenzene and persulphate, with the results shown in Fig. 4. The superiority of k_1 over k in respect of dependence on initial concentration (cf. Figs. 2 and 4) is sufficient perhaps to indicate that the approach outlined is sound. A more satisfactory test would have been possible if sufficient data had been available at the higher temperatures, but unfortunately it was not possible to obtain a satisfactory evaluation of the necessary quantities with the data recorded for these temperatures.

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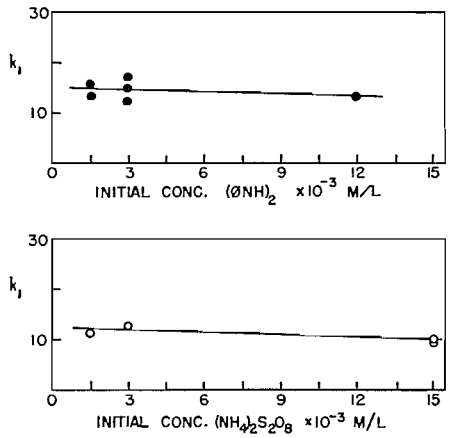

FIG. 4. Effect of different concentrations of hydrazobenzene on k_1, the corrected rate constant.
Temp. 25.02°C.
Upper frame: Initial concentration ammonium persulphate, 0.00600 mole/liter.
Lower frame: Initial concentration hydrazobenzene, 0.00600 mole/liter.

The second order kinetics displayed in individual experiments for considerable variation in initial concentrations of reactants would indicate that a compensation existed in the reaction to modify the behavior predicted by the relation $k \propto \sqrt{[P]/[H]}$. It is inherent in this relation that in a given experiment, unless the reactants are in equimolar concentrations, the calculated specific rate should decrease during the course of reaction when hydrazobenzene is in excess and increase when persulphate is in excess. Actually, the deviations from linearity were always in the direction of apparent increase in specific rate. Much of the compensation might have been due to an increased dissociation of persulphate as its consumption progressed, but it seems likely that some other factor or factors not yet identified also contributed to the observed behavior.

The interpretation of the experimental data suggests that the reaction is initiated by the formation of sulphate ion radicals resulting from direct attack by persulphate ions rather than by sulphate ion radicals from unimolecular decomposition of persulphate.

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PREPARATION AND PROPERTIES OF CRYSTALLINE CANDIDIN[1]

By L. C. Vining and W. A. Taber

ABSTRACT

Candidin, the antifungal antibiotic produced by *Streptomyces viridoflavus*, has been isolated in crystalline form. Analyses and equivalent weight values best fit a molecular formula $C_{46}H_{75}NO_{17}$. The substance is amphoteric and probably contains one carboxyl and one amino group. Infrared spectral evidence also indicates a polyhydroxylated structure, and the absorption in the visible region shows the presence of a conjugated heptaene chromophore. An additional conjugated diene elsewhere in the molecule is suggested by hydrogenation values and the absorption maximum at 228 mμ.

The isolation from *Streptomyces viridoflavus* of a new antibiotic active primarily against fungi was first reported in 1953 (5). The light absorption spectrum and chemical properties of this substance were very similar to candicidin (2), but it was shown to differ both in its behavior upon countercurrent distribution, and by the higher activity exhibited against filamentous fungi.

Subsequently both candidin and candicidin were recognized (3) as members of a large group of antibiotics, isolated from various *Streptomyces* species. These antibiotics possess in common a high and selective activity against fungi, a general similarity in chemical properties, and a typical three-peaked absorption spectrum revealing the presence within the molecule of a conjugated polyene chromophore containing from four to seven double bonds. A more detailed comparison between candidin and three other members of the group possessing a heptaene chromophore demonstrated (6) that candidin was different, not only from candicidin, but also from ascosin and trichomycin.

A method for the production of candidin in shaken flasks has been described (5). Using stirred tanks, maximum broth activity was attained more rapidly and was considerably higher. The antifungal component was concentrated and the crude solid containing about 50% of candidin was extracted with hot 70% aqueous ethanol to remove the bulk of the impurities. Final purification was achieved by crystallization from a methanol–chloroform–water mixture.

Candidin was obtained as golden-yellow needles which are insoluble in water and most organic solvents. It is relatively soluble in glacial acetic acid, pyridine, and dimethylformamide, and somewhat soluble in many polar solvents such as alcohols, dioxane, or acetone when they are diluted with up to 40% of water. It can be readily dissolved in dilute aqueous mineral acids or sodium hydroxide but not in sodium carbonate. The presence of both basic and acidic groups was confirmed by titration when neutralization equivalents

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of 928 and 922 were obtained respectively. In acidic solution, candidin is rapidly degraded with loss of the characteristic absorption spectrum, but only a slight loss of activity was detected after four hours in 0.01 *N* sodium hydroxide.

Stable, water-soluble preparations of the antibiotic have been obtained (5, 6) by freeze-drying aqueous solutions at neutral or slightly alkaline pH. Two such fractions, differing in their absorption spectra in neutral aqueous solution, were reported. The less active of these, candidin A, showed a three-peaked spectrum with maxima at 365, 384, and 408 mμ, typical of a conjugated heptaene. The second fraction, candidin B, gave only a single intense absorption maximum at 335–345 mμ. Paper chromatography and counter-current distribution studies have demonstrated, however, that the same antifungal factor is responsible for the activity of the two fractions, and the difference in spectral properties has now been accounted for. Although candidin itself is insoluble in water, neutral freeze-dried preparations containing a mixture of candidin and its sodium salt readily disperse in water to clear "solutions" which are remarkable in possessing only a single intense absorption maximum at 335–345 mμ. If the candidin is brought into true solution, either by adjusting with sodium hydroxide, mineral acid, or by diluting with ethanol, the absorption spectrum reverts to that of a typical conjugated heptaene. The failure of candidin A to show a typical spectral change in neutral aqueous solution was due to the solubilizing action of the large amounts of impurity present in the sample. Lowering the solubility by the addition of sodium chloride was sufficient to effect the conversion to a spectrum showing a single peak of absorption at 335 mμ.

Crystalline candidin does not melt, but darkens slowly above 180° C. Microanalytical data indicate a molecular formula of $C_{46}H_{75}NO_{17}$. No methoxyl or acetyl groups were found, but a Kuhn–Roth determination suggests the presence of six C-methyl groups. Candidin was optically active and gave α_D^{27}° C. = +363° (*c* = 0.3 in dimethylformamide); +205° (*c* = 0.3 in glacial acetic acid).

The absorption spectrum in the ultraviolet and visible regions is shown in Fig. 1. Exposure of an alcoholic solution containing catalytic amounts of iodine to strong light does not bring about any change in the wavelengths or intensity of the maxima and it is concluded that the conjugated heptaene is present in the all-*trans* configuration.

The infrared absorption spectrum of candidin is shown in Fig. 2. The strong broad band at 3400 cm.$^{-1}$ together with two intense peaks at 1040 and 1070 cm.$^{-1}$ suggest a polyhydroxy compound, accounting for the high proportion of oxygen in the molecule. The band at 1385 cm.$^{-1}$ can probably be assigned to the C-methyl groups indicated by the Kuhn–Roth determination, while the presence of amino and carboxyl groups is confirmed by the bands at 1555 and 1705 cm.$^{-1}$ respectively. A second band in the carbonyl region at 1715 cm.$^{-1}$ is suggestive of a ketone, but tests with 2,4-dinitrophenylhydrazine, semicarbazide, and Schiff's reagent were negative. Bands at 840, 970, 1015,

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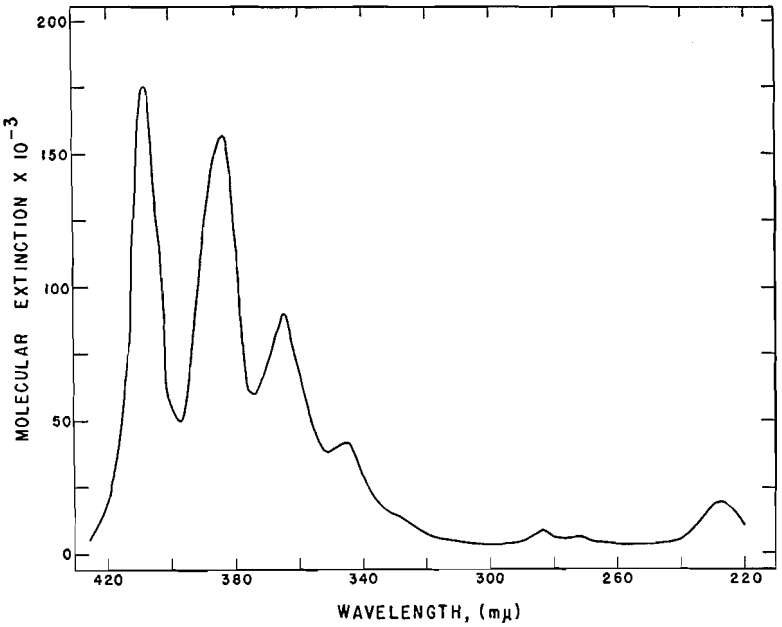

FIG. 1. Absorption spectrum of candidin in ethanol.

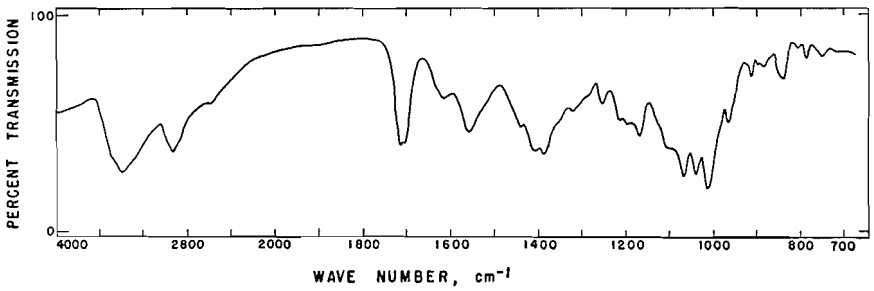

FIG. 2. Infrared absorption spectrum of candidin (pressed potassium bromide pellet).

and 1620 cm.$^{-1}$ are provisionally assigned to the unsaturated groups in the molecule.

Upon hydrogenation under conditions where only carbon to carbon double bonds are reduced, candidin rapidly took up nine moles of hydrogen. The molecule must, therefore, contain two unsaturated groups in addition to the conjugated heptaene chromophore. In view of the absorption maximum in the ultraviolet region at 228 mμ, these are probably present as a conjugated diene.

The antifungal activity of candidin preparations increases with increasing purity. A sample of the crystalline material assayed against *Candida albicans* ATCC 10231 by the cup diffusion method (4) gave a potency of 15,000 units per mgm.

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EXPERIMENTAL

Production and Isolation

Candidin was produced on a small scale in a 5 gal. stirred tank. Fifteen liters of medium were inoculated with a shake culture of *S. viridoflavus* as described previously (5) and incubated for four days at 28° C. The whole broth was then adjusted to pH 4.5 with conc. HCl, 2% by weight of filter aid (HyFlo–supercel) stirred in, and the solids separated. They were extracted twice with 10 liters of 70% aqueous ethanol at 50° C., and the extract concentrated under vacuum to 1 liter. The precipitated candidin was separated by centrifugation, washed thoroughly first with 25% aqueous methanol, then with acetone, and dried to yield crude amorphous yellow powder (7.7 gm.) containing 58% candidin.

On a larger scale, candidin was produced in a 150 gal. tank. It was then found more convenient to carry out an initial concentration of the broth to half volume, and dilute with ethanol to a concentration of 70%. The filtered aqueous ethanolic solution was then worked up as described above to give 45 gm. of a crude preparation containing 50% candidin.

Crystallization of Candidin

The crude product (10 gm.) was extracted for 30 min. on a steam bath with hot 75% ethanol (500 cc.). The insoluble residue was extracted by shaking under nitrogen for two hours with a mixture of methanol (1 liter) and chloroform (800 ml.), filtered, and the filtrate diluted with distilled water (400 ml.) and petroleum–ether (400 ml.). The upper layer was separated and slowly evaporated with a stream of nitrogen, when candidin was precipitated as fine needles (600 mgm.). A sample was dried at 25° under phosphorus pentoxide *in vacuo*. Found: C, 60.20; H, 8.24; N, 1.52; *C*—Me, 9.98%. Calc. for $C_{46}H_{75}NO_{17}$: C, 60.44; H, 8.27; N, 1.53; 6*C*—Me, 9.77%.

Further crops of crystalline material could be obtained by repeated extraction of the residual material with the methanol–chloroform mixture.

Neutralization Equivalent

Candidin was titrated as a base in glacial acetic acid with perchloric acid, using crystal violet indicator. The neutralization equivalent was 928.

The acid group in candidin was titrated potentiometrically in dimethylformamide with 0.05 *N* NaOH. The neutralization equivalent was 922. The calculated value for a formula $C_{46}H_{75}NO_{17}$ is 914.

Hydrogenation

Candidin was hydrogenated at atmospheric pressure and room temperature in a microhydrogenation apparatus. Both dimethylformamide and glacial acetic acid were used as solvents, and 5% palladium on carbon, Adams catalyst, and palladium oxide on barium sulphate (1) were used as catalysts. The hydrogenation equivalent was 102 (±5) under all conditions.

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THE SUGAR COMPONENT OF DEOXYRIBONUCLEOSIDES[1]

By I. G. Walker and G. C. Butler

ABSTRACT

From highly polymerized deoxyribonucleate the nucleosides have been isolated by an improved method. The sugar obtained on hydrolysis of the individual nucleosides has been shown to be D-2-deoxyribose in each case.

INTRODUCTION

Although it is assumed that the only carbohydrate constituent of deoxyribonucleate (DNA) is D-2-deoxyribose, the sugar has not been isolated from all of the five nucleosides known to be present in most samples of DNA. Levene and Mori (16) obtained a guanine nucleoside after digestion of calf thymus DNA and concluded that it was a glycoside of D-2-deoxyribose (15). Subsequently other workers found that the same sugar was liberated on acid hydrolysis of the mixed purine deoxynucleosides (6, 10, 12). Similar studies of the pyrimidine deoxynucleosides have been unsuccessful because of the difficulty of cleaving the glycosidic linkages without destroying the sugar.

The results obtained by MacNutt (19) and Friedkin and Roberts (8) in their experiments with nucleoside phosphorylase have provided good evidence that the same sugar is present in the purine—and pyrimidine—deoxynucleosides.

Burke (3) reported, without giving experimental details, that reduction with sodium and ethanol in liquid ammonia rendered pyrimidine nucleosides easily hydrolyzable by Dowex 50 cation exchange resin. The sugars liberated from thymidine and deoxycytidine were identified with D-2-deoxyribose by chromatography and ionophoresis on paper.

In spite of all this evidence we considered that it would be worth while to isolate and to identify in the conventional way the sugar from each of the nucleosides of DNA.

Highly polymerized DNA (20) was hydrolyzed by the combined actions of pancreatic deoxyribonuclease (18) and the phosphodiesterase and 5′-nucleotidase of water moccasin venom. The resulting nucleoside mixture was resolved by anion exchange chromatography (1). Two difficulties were encountered at this stage. The first of these was the finding that the nucleosides of cytosine and 5-methylcytosine did not separate during the chromatography. Therefore, to prepare each of these free of the other the corresponding nucleotides were separated and isolated and from them the nucleosides obtained by hydrolysis with phosphomonoesterase. The second difficulty was that of isolating crystals of the other nucleosides from the large volumes of salt solutions in which they were eluted from the ion exchange column. This problem was solved by our discovery, in common with others (4, 17), that nucleosides and nucleotides were readily adsorbed from aqueous solutions on passage through a column of activated charcoal. When this procedure was applied to the eluates from

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the ion exchange columns the nucleosides were retained quantitatively on the charcoal column and the salt passed through. The nucleoside (or nucleotide) could be eluted from the charcoal easily with ammoniacal alcohol. Good yields of the nucleosides were obtained and their physical constants agreed well with the most recently reported values (1, 7, 19).

The purine nucleosides deoxyadenosine and deoxyguanosine were most conveniently hydrolyzed by an aqueous suspension of a sulphonic acid cation exchange resin in the hydrogen form (11), the times and temperatures being selected to give a maximum color development when the quantitative Schiff's test (5) was applied to the supernatant solution.

The pyrimidine nucleosides were reduced prior to hydrolysis since Levene and La Forge (13) had demonstrated that ribose could be obtained from uridine by mild acid hydrolysis following catalytic hydrogenation of the nucleoside. Levene and London (14), however, reported that their efforts to hydrogenate thymidine, in the same manner as uridine, were unsuccessful. In our experiments deoxycytidine readily absorbed one mole of hydrogen in the presence of palladium black; the product, on acid hydrolysis, yielded a reducing sugar and dihydrouracil. This was expected since Brown and Johnson (2) had found that cytosine was deaminated on catalytic hydrogenation. Under the same conditions thymidine absorbed two moles of hydrogen and was converted to a substance that did not liberate any reducing or Schiff-positive material on heating with 0.1 *N* or 1.0 *N* sulphuric acid at 100° for periods up to 90 min. This experience made it necessary to use other methods of reducing thymidine, and sodium amalgam was found to be suitable for the purpose. The reduction product in this case was readily amenable to acid hydrolysis.

The hydrolytic conditions needed to free the pyrimidine-bound sugars were harsher than those used for the purine nucleosides. In order to avoid possible chemical changes brought about by this treatment and the preliminary reduction, thymidine and deoxycytidine (after deamination to deoxyuridine) were hydrolyzed with the thymidine phosphorylase system of Friedkin and Roberts (8).

The sugars, liberated by the procedures described above from each of the four nucleosides, were compared with each other and with synthetic L-2-deoxyribose (21) by paper chromatography in two different solvent systems and by the melting points, mixed melting points, and rotations of their crystalline benzylphenylhydrazones. In each of the four cases it was concluded that the sugar was D-2-deoxyribose.

EXPERIMENTAL

All distillations at reduced pressure were carried out with a bath temperature not exceeding 40°.

Isolation and Characterization of the Deoxynucleosides

Twenty grams of DNA, prepared by the method of Marko and Butler (20), was dispersed in 500 ml. of water and hydrolyzed with 150 mgm. of deoxyribonuclease (18). When hydrolysis was complete, the pH of the solution was

adjusted to 9.0 with conc. ammonium hydroxide, and 500 mgm. of lyophilized water moccasin venom,* dissolved in 10 ml. of water, was added. The digest was incubated at 37° and maintained at pH 9.0 by the periodic addition of 2 *N* ammonium hydroxide. When the pH of the digest ceased to fall (4–6 hr.) the addition of ammonium hydroxide was stopped and the digest stored at 37° overnight. After this treatment, analyses usually showed that 70–80% of the total phosphorus of the digest had become inorganic phosphate. In order to carry the release of nucleosides nearer to completion, magnesium formate (equivalent to the phosphate content) was added and the precipitated magnesium ammonium phosphate removed by centrifugation. More of the venom (200 mgm.) was added to the supernatant solution which had been readjusted to pH 9.0, and the mixture was stored at 37° for 15 hr.

The resulting solution was reduced to a volume of 200 ml. by distillation *in vacuo*, brought to pH 10.4 with conc. ammonium hydroxide, and poured onto a column (17 cm. height × 6.8 cm. diameter) of Dowex 2 (200–400 mesh) in the formate form. The flow rate throughout the chromatography was 150 ml. per hr. Each fraction was collected for 30 min. and its nucleoside content measured by ultraviolet spectrophotometry. The procedure and results may be summarized as follows:

Fraction	Nucleoside of	Eluent	Volume (l.)
I	Adenine and cytosine	0.02 *M* formate, pH 9.8	2
II	Thymine	0.05 *M* formate, pH 8.5	2
III	Guanine	0.05 *M* formate, pH 4.5	3

The first of these eluents was prepared by dissolving 0.02 mole of formic acid in 750 ml. of water, adding ammonium hydroxide until the pH was 9.8, adjusting the volume to one liter, and finally readjusting the pH to 9.8 with ammonium hydroxide. The other eluents were prepared by a similar procedure.

After reduction to a volume of 50 ml. by vacuum distillation Fraction I was stored at 5° for 24 hr. Most of the deoxyadenosine crystallized and yields of 1.9–2.0 gm. were obtained. When it was recrystallized from water this material had: nitrogen content, 23.1% (calculated for $C_{10}H_{13}O_3N_5.3H_2O$, 23.0%); m.p. 187.5–189°; $[\alpha]_D^{21}$, −32° (c = 1.11 in water at pH 7.0).

The mother liquors and washings of the deoxyadenosine crystals were combined, adjusted to pH 4.5 with formic acid, and chromatographed on a column of carboxyl cation exchange resin (Amberlite IRC 50, 500 mesh). The column measured 20 cm. in height by 3.4 cm. in diameter and was prepared by washing it with a 0.5 *M* solution of ammonium formate of pH 4.5 followed by water to remove the buffer. After the nucleoside solution had passed into the resin, elution was carried out with 0.05 *M* ammonium formate (pH 4.5) at the rate of 80 ml. per hr. By collecting 60 ml. samples it was found that deoxycytidine was eluted in a volume of 700 ml. followed closely by deoxyadenosine.

**Purchased from Ross Allen's Reptile Institute, Silver Springs, Florida.*

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The deoxycytidine solution was passed through a column containing 10 gm. of activated charcoal* and the column washed with 50 ml. of water to remove salt. Elution of the nucleoside from the charcoal was effected with 200 ml. of ammoniacal alcohol (prepared by mixing 500 ml. of 95% ethanol, 430 ml. of water, and 17 ml. of conc. ammonium hydroxide). The resulting filtrate was distilled to dryness under reduced pressure and the residue dried to a fluffy white solid by the repeated vacuum distillation of 10 ml. portions of absolute ethanol. In order to crystallize the deoxycytidine it was converted to the hydrochloride by dissolving the dry residue in 7 ml. of methanol and adding a solution of dry hydrogen chloride in methanol (15 ml. of 3 *N*). Crystallization began almost immediately and after storing at 5° overnight 780 mgm. of crystals were collected. This hydrochloride was recrystallized by dissolving it in 1 ml. of hot water and slowly adding 3 ml. of ethanol. In a melting-point determination the crystals turned brown at 168° and melted with decomposition at 174°. The nitrogen content was 15.8%; calculated for $C_9H_{14}O_4N_3.HCl$, 15.9%. The optical rotation was $[\alpha]_D^{24} = +54.3°$ (in water at pH 7.0, $c = 5.51$ calculated as the free nucleoside).

Fraction II was distilled *in vacuo* to a volume of about 10 ml. On storing this solution at 5°, thymidine crystallized in yields of 1.6 to 2.0 gm. After recrystallization from water the thymidine had: nitrogen content, 10.2% (calculated for $C_{10}H_{15}O_5N_2.2H_2O$, 10.1%); m.p. 189–190°; $[\alpha]_D^{21}$, +18° ($c = 1.16$ in water at pH 7.0).

Fraction III was passed through 15 gm. of charcoal in a column 3.4 cm. in diameter and the column washed with water. Deoxyguanosine was eluted with 1 liter of ammoniacal alcohol. After the volume of the filtrate was reduced to 400 ml. by vacuum distillation and it was stored at 5°, 1.4 gm. of nucleoside crystallized as fine needles. Concentration of the mother liquors yielded another 0.6 gm. After recrystallization from water the deoxyguanosine had: N, 24.3% (calculated for $C_{10}H_{13}O_4N_5.1\frac{1}{4}\ H_2O$, 24.2%); no m.p. up to 250°; $[\alpha]_D^{24}$, −40° ($c = 0.924$ in 0.1 *N* NaOH, pH 12.64).

In order to prepare deoxycytidine free of the 5-methylcytosine nucleoside it was found convenient to dephosphorylate chromatographically pure deoxycytidine-5′-phosphate. Deoxycytidylic acid (310 mgm.) was dissolved in 35 ml. of water and the pH of the solution adjusted to 9.0 with sodium hydroxide. On treatment with 10 mgm. of water moccasin venom for 30 hr. at 38°, all of the phosphorus in the solution had become inorganic. The digest was acidified to pH 5.0 with glacial acetic acid and passed through 3 gm. of charcoal in a column of 2.5 cm. diameter. After the column was washed with 10 ml. of water the nucleoside was eluted with 100 ml. of the ammoniacal ethanol. This eluate was evaporated to dryness and the residue dried by distilling from it 20 ml. portions of absolute ethanol. The residue was dissolved in 5 ml. of methanol and the solution clarified by centrifugation. After 3 ml. of 3 *N* hydrogen chloride in methanol was added to the clear supernatant solution crystals began to appear immediately and 180 mgm. were collected following storage at 5° for a few hours. An additional 35 mgm. of crystals was obtained from the mother

**Darco G–60, Atlas Powder Co.*

liquors. The combined product was recrystallized by dissolving it in 0.15 ml. of hot water, slowly adding 2 ml. of absolute ethanol, and chilling. The resulting crystals showed browning at 167° and melted with decomposition at 171°.

When the procedure just described was applied to 110 mgm. of chromatographically pure 5-methyldeoxycytidylic acid, 59 mgm. of 5-methyldeoxycytidine hydrochloride (m.p. 157–158°) was obtained.

Isolation of the Sugar Component of the Purine Deoxynucleosides

Deoxyguanosine (600 mgm.), 2.4 gm. of dry Nalcite HCR*, and 11 ml. of water were mixed in a 15 ml. centrifuge tube and heated at 80° for 10 min. with stirring. The resin was collected by centrifuging and washed three times with small portions of water. Traces of sulphuric acid were removed from the combined supernatant and wash solutions by treatment successively with two drops of 3 *N* barium hydroxide and a small pellet of dry ice. The filtrate obtained from this mixture was concentrated to a sirup *in vacuo* at room temperature.

The sirup was transferred to a 30 ml. beaker with 2 ml. of water and to it were added 300 mgm. of sodium acetate (trihydrate) and 528 mgm. of recrystallized benzylphenylhydrazine hydrochloride dissolved in 4 ml. of β-methoxy-ethanol (methyl cellosolve). The solution was thoroughly mixed and water added to it dropwise with mixing until an opalescence appeared. After storage in the cold the yellow crystals were collected by filtration and washed with methyl cellosolve – water (2 : 1). A final washing with ether removed much of the yellow color leaving 323 mgm. of light yellow needles with m.p. 118–124°. The crude product was purified by dissolving it in the minimum volume of methyl cellosolve, adding two volumes of ether, and storing the solution in the cold. After collection by filtering the white needles that separated melted at 127–128°.

Treatment of deoxyadenosine (600 mgm.) in a similar manner yielded 400 mgm. of crude benzylphenylhydrazone which on recrystallization from methyl cellosolve – ether gave 215 mgm. of white crystals with m.p. 126–128°.

Isolation of the Sugar Component of Deoxycytidine

Deoxycytidine hydrochloride (645 mgm.) was dissolved in 50 ml. of water and the solution neutralized with sodium hydroxide solution. Palladium black (500 mgm.) was added and the hydrogenation allowed to proceed for $3\frac{1}{2}$ hr. at 75° with a hydrogen pressure slightly above atmospheric. The uptake of hydrogen ceased at one mole per mole of nucleoside. After removal of catalyst the solution, now alkaline because of the ammonia released on deamination(2), was neutralized with hydrochloric acid. The nucleoside was adsorbed from the solution by passing it through 9 gm. of charcoal in a column 3.4 cm. in diameter. The column was washed with water to remove salts and the nucleoside eluted with 200 ml. of water: ethanol (1: 1). Solvent was distilled from the eluate, the sirupy residue was dissolved in 20 ml. of 0.1 *N* sulphuric acid, and

**Cation exchange resin converted to the hydrogen form with sulphuric acid, washed with water, and dried in air.*

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the solution heated under reflux in a boiling water bath for 30 min. The solution was cooled, neutralized with barium hydroxide, filtered with the aid of a little charcoal, and distilled to dryness *in vacuo*. The residue was dissolved in methanol to give a solution which on slow evaporation deposited crystalline dihydrouracil of m.p. 272° (Lit. (9) 272–274°). From the sugar remaining in the methanol a benzylphenylhydrazone was prepared, two such experiments yielding 180 mgm. of crude product which had m.p. 127–129° after recrystallization from methyl cellosolve – ether.

Isolation of the Sugar Component of Thymidine

Thymidine (400 mgm.) in 10 ml. of water was stirred for two hours with 3 gm. of sodium–mercury amalgam (2.5% sodium). A further 3 gm. of amalgam was added and the stirring continued until all the sodium had reacted. After a further treatment with 3 gm. of fresh amalgam the solution had a low optical density at 2670 Å indicating that reduction of the pyrimidine ring was almost complete. After being filtered the solution was neutralized with 1 *N* sulphuric acid and poured into 10 times its volume of ethanol: ether (4: 1). The precipitated sodium sulphate was removed by filtration and ethanol and ether removed from the filtrate by vacuum distillation. The aqueous solution remaining was adjusted to 20 ml., made $\frac{1}{10}$ *N* with sulphuric acid, and heated at 100° under reflux for 30 min. The sirupy residue left after removal of sulphuric acid and water yielded 135 mgm. of crude benzylphenylhydrazone which on recrystallization from methyl cellosolve – ether had m.p. 127–129°. No dihydrothymine was isolated in these preparations and subsequent experiments showed that it was destroyed in alkaline solution.

Enzymatic Hydrolysis of Deoxycytidine and Thymidine

The enzyme thymidine phosphorylase was extracted from fresh rat liver as described by Friedkin and Roberts (8) but the purification was not carried beyond the first fractionation with ammonium sulphate.

Thymidine (1.8 mM.) was dissolved in 50 ml. of 0.1 *M* arsenate – 0.1 *M* succinate buffer of pH 5.9 and added to 100 ml. of enzyme solution. After incubation of the mixture at 38° for 16 hr. spectrophotometric assay (8) indicated complete arsenolysis of the nucleoside. A protein precipitate was removed by centrifugation and the remainder of the protein in solution was precipitated by the addition of one-tenth volume of 3% perchloric acid and centrifuging. The combined supernatant solution and water washings of the precipitate were reduced to a volume of 50 ml. by vacuum distillation and desalted by passage in turn through a 50 cc. bed of Nalcite HCR (H form) and 50 cc. of Dowex 1 (Acetate form). The dry residue, obtained from the effluent solution by distillation, was converted to the benzylphenylhydrazone in the usual manner. The recrystallized product weighed 140 mgm. and had m.p. 126–128°.

Thymidine phosphorylase acts upon thymidine and deoxyuridine but not upon deoxycytidine. Consequently, to obtain the sugar from this last nucleoside it was deaminated by the method of MacNutt (19) before treatment with the enzyme. Thus 1.6 mM. of deoxyuridine yielded 83 mgm. of recrystallized sugar benzylphenylhydrazone with m.p. 126–128°.

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Specific Rotations of the Benzylphenylhydrazones

The optical rotations of the benzylphenylhydrazones, prepared as described in the foregoing, were measured in pyridine solution and compared with that of the same derivative of synthetic L-2-deoxyribose (21) which derivative had m.p. 126–128°. The results are to be found in Table I.

TABLE I

A COMPARISON OF THE OPTICAL ROTATIONS OF THE BENZYLPHENYLHYDRAZONES DERIVED FROM THE DEOXYNUCLEOSIDE SUGARS AND SYNTHETIC L-2-DEOXYRIBOSE

Benzylphenylhydrazone derived from	Method of preparation of sugar	Specific rotation in pyridine		
		Temp. (°C.)	Concn. (%)	$[\alpha]_D^t$
Deoxyguanosine	Resin hydrolysis	20	3.5	−19°
Deoxyguanosine	Resin hydrolysis	18	3.0	−18°
Deoxyguanosine	Resin hydrolysis	23	2.5	−16°
Deoxyadenosine	Resin hydrolysis	24	4.2	−20°
Deoxyadenosine	Resin hydrolysis	20	3.5	−17°
Deoxycytidine	Catalytic hydrogenation and acid hydrolysis	27	4.6	−17°
Deoxycytidine	Enzymatic hydrolysis	28	4.2	−16°
Thymidine	Amalgam reduction and acid hydrolysis	24	4.7	−19°
Thymidine	Amalgam reduction and acid hydrolysis	20	2.3	−15°
Thymidine	Enzymatic hydrolysis	25	5.4	−18°
Synthetic L-2-deoxyribose		18	4.0	+21°
Synthetic L-2-deoxyribose		21	3.0	+20°

Comparison of Sugars by Paper Chromatography

Two solvent systems were used: (*a*) butanol, pyridine, water, 8:2:1, and (*b*) butanol, ethanol, water, 4:1:1. Chromatograms on Whatman No. 3 paper were developed upwards until the solvent front had reached a height of 15 cm. This needed 1.5 hr. for system (*a*) and 2 hr. for system (*b*). After development the papers were dried in a warm oven, sprayed with a 2% solution of *m*-phenylenediamine hydrochloride in 75% ethanol (6), and heated at 100° for 5 min. The positions of the sugars were indicated by spots fluorescing under ultraviolet light.

The following sugars were compared by simultaneous chromatography:

1. Two samples obtained from the hot acid (resin) hydrolysis of deoxyadenosine and deoxyguanosine.
2. Two samples from the enzymatic arsenolysis of thymidine and deoxyuridine.
3. One sample from the hot acid hydrolysis of reduced thymidine.
4. Glucose.
5. Arabinose.
6. L-2-Deoxyribose.

The R_f values so obtained were:

With system (*a*): All nucleoside sugars and L-2-deoxyribose, 0.43; glucose, 0.14; arabinose, 0.22.

With system (*b*): All nucleoside sugars and L-2-deoxyribose, 0.43; glucose, 0.23; arabinose, 0.34.

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THE LIMITING HEAT OF SOLUTION OF PLUTONIUM IN SOME RARE EARTH METALS[1]

By D. E. McKenzie, W. M. Jenkinson, and A. S. Denovan

ABSTRACT

The distribution of plutonium between neutron-irradiated uranium and some rare earth metals has been examined as a function of temperature in the range 1160° to 1350°C. The results are used to calculate $\bar{L}°_{Pu}$, the limiting partial molal heat content of plutonium, at 1250°C. in lanthanum, cerium, neodymium, and a commercial preparation of mixed rare earths (misch metal). The following values (in kilocalories) were obtained: lanthanum 2.9, cerium 1.1, neodymium 0.0, and misch metal 1.1. The maximum error associated with these values is ±0.4 kilocalories.

INTRODUCTION

In a previous paper (2) the limiting heat of solution of plutonium in liquid silver was determined. The method consisted of measuring the effect of temperature on the distribution of plutonium between neutron-irradiated uranium and silver. Similar measurements have been made during a study of the distribution of plutonium between uranium fuel and some rare earth metals. The data on plutonium distribution as a function of temperature have been used to calculate values for the heat of solution of plutonium in lanthanum, cerium, neodymium, and a commercial preparation of mixed rare earths (misch metal). The results are presented in this paper. Experiments in which lanthanum and cerium were used as extractants for plutonium have been reported by Spedding and co-workers of the Ames laboratory of the United States Atomic Energy Commission (5).

EXPERIMENTAL

Materials and Apparatus

The neutron-irradiated uranium was cut from rods which had been irradiated in the NRX reactor and allowed to decay for three years. The concentration of plutonium in this material was 0.025%. The purities of the lanthanum, cerium, and neodymium, which were obtained from A. D. MacKay, Inc. as metal billets, are given in Table I. Table I lists, also, the materials other than rare earths in the misch metal (New Process Metals Inc.). The approximate

TABLE I

Analyses of extractants

Extractant	Major component	Impurities
Lanthanum	97–98% La	Other rare earth metals
Cerium	98.6% Ce	Other rare earth metals
Neodymium	99% Nd	Other rare earth metals
Misch metal	98% rare earths	1.32% Fe, 0.58% Mg, 0.09% silica

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percentages of the rare earths in this preparation are as follows: cerium 50–55%, lanthanum 20–25%, neodymium 15–20%, praseodymium 5–7%, and other rare earth metals 2–5%.

The metals were contacted in beryllia or alumina crucibles. The beryllia crucibles were obtained from the Atomic Energy Research Establishment, Harwell, England; the alumina crucibles ('Triangle' recrystallized alumina) were obtained from The Morgan Crucible Co. Ltd.

The uranium and rare earth metal were heated by a tungsten wire coil surrounded by thermal and radiation shields. The assembly was mounted in a glass bulb which could be evacuated by diffusion and mechanical pumps.

Temperatures were measured with a platinum, platinum 10% rhodium thermocouple which was coiled in the heating zone as a seat for the crucible containing the charge. The thermocouple was calibrated to give the temperature of the charge by melting various pure metals, in the appropriate crucible, in the apparatus. The calibration was checked frequently, generally after three runs. The temperatures are considered to be accurate to $\pm 5°$ C.

Procedure

For an experiment, weighed amounts of neutron-irradiated uranium and a rare earth metal in the oxide crucible were placed in the apparatus. The uranium had been etched in acid to remove approximately 25% of its weight for a reference solution, then washed in water and acetone. The glass bulb was pumped down to a pressure of 10^{-5} mm. of Hg or less before admitting welding grade argon to a pressure of one atmosphere. The charge was then heated to temperature and held for 20 min., which was found to be ample time to establish equilibrium.

After equilibration the melt was essentially quenched by shutting off the power since the uranium phase solidified in about 15 sec. even for experiments at the highest temperatures. The metal billet, after further cooling in argon, was removed from the crucible and the two phases separated mechanically. In all cases the complete phase, after weighing, was dissolved for analyses.

Analyses

The phases were analyzed for plutonium by the direct counting of thin sources prepared from the solutions. For each run at least two determinations, on separate days, were made of the ratio of α counts due to plutonium in the two phases. This ratio was checked for some experiments by analyzing for plutonium using the LaF_3 procedure.

The distribution coefficient for plutonium, K_{Pu}, was calculated from the expression

$$K_{Pu} = \frac{\text{Pu counts in rare earth}}{\text{Pu counts in uranium}} \times \frac{\text{moles of uranium}}{\text{moles of rare earth}} .$$

There is negligible error in assuming that this K_{Pu} is the ratio of the mole fraction of Pu in rare earth to the mole fraction of Pu in uranium. In making these calculations for the misch metal runs the atomic weight of cerium was used to calculate the number of moles of misch metal.

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RESULTS AND DISCUSSION

The results are summarized in Table II. The runs in which lanthanum or neodymium was the extractant were made using beryllia crucibles. The first two cerium runs were performed in beryllia crucibles but alumina was used for the remainder. Liquid cerium at temperatures above 1200° C. appeared to wet and seep through the beryllia crucibles. All experiments with misch metal were carried out in alumina containers.

Plutonium distributions at 1200° C. have been obtained for the systems La–U and Ce–U at the Ames laboratory (5). In the Ames work two different

TABLE II

DATA FOR THE DISTRIBUTION OF PLUTONIUM
Initial Pu concn. = 0.025%

Extractant	Temp. (°C.)	Wt. U (gm.)	Wt. ext. (gm.)	Pu ratio* (ext./U)	K_{Pu}
La	1160	3.8553	4.5516	0.682	0.337
	1170	4.2390	4.3000	0.600	0.345
	1205	4.0230	4.0806	0.608	0.350
	1243	4.0485	4.4262	0.669	0.357
	1276	3.7839	3.7946	0.629	0.366
	1310	3.9280	4.0400	0.661	0.375
	1325	4.3172	4.8266	0.721	0.376
Ce	1160	3.4927	3.4463	0.892	0.532
	1200	4.0471	4.0823	0.917	0.535
	1250	3.9108	4.3846	1.035	0.543
	1300	4.5153	4.7902	0.993	0.551
	1330	3.8892	4.2914	1.031	0.550
	1350	3.7774	3.9650	0.995	0.558
Nd	1160	4.0560	4.6804	0.936	0.491
	1200	3.8435	4.0958	0.853	0.484
	1250	4.0620	4.1406	0.822	0.488
	1250	4.1038	4.0768	0.798	0.486
	1300	4.5446	4.8170	0.858	0.490
	1300	4.0840	4.1413	0.818	0.488
	1350	3.9100	3.8994	0.803	0.487
Misch metal	1160	3.9115	4.1663	0.807	0.446
	1200	3.8281	3.9717	0.790	0.448
	1250	4.3880	4.4115	0.775	0.454
	1300	4.3491	4.2841	0.768	0.459
	1350	4.1323	3.9633	0.756	0.464
	1350	4.2680	4.5114	0.837	0.466

**Average of at least two determinations.*

TABLE III

COMPARISON OF PLUTONIUM DISTRIBUTIONS AT 1200°C. FOR THE SYSTEMS La–U AND Ce–U

Extractant	Initial Pu conc. in U (%)	K_{Pu}	
		Ames (5)	Chalk River
La	0.023	0.326	0.350
	0.0018	0.379*	
Ce	0.023	0.600	0.535
	0.0018	0.559	

**Average of two runs.*

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samples of uranium, of plutonium concentrations 0.023% (i.e. the same as in this study) and 0.0018%, were used. The results are compared with those of this work in Table III.

The distribution data are plotted as log K_{Pu} vs. $1/T$ in Fig. 1. The straight lines of Fig. 1 were obtained from a least squares treatment of the data which yielded the following equations:

Lanthanum, $\log K_{Pu} = -0.0302 - 629/T$;
Cerium, $\log K_{Pu} = -0.105 - 243/T$;
Neodymium, $\log K_{Pu} = -0.315 + 5.3/T$;
Misch metal, $\log K_{Pu} = -0.190 - 232/T$.

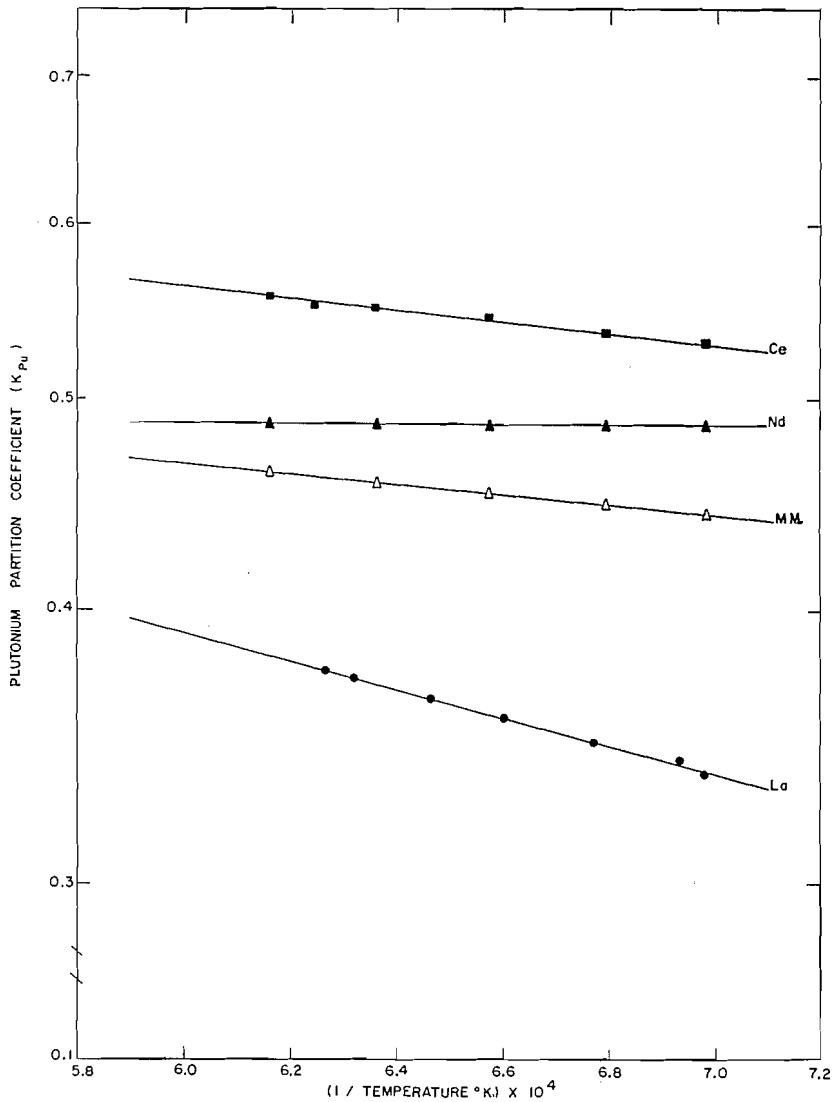

FIG. 1. The effect of temperature on the distribution of plutonium between neutron-irradiated uranium and some rare earth metals. Uranium/rare earth weight ratio = 1/1. Initial concentration of plutonium in uranium = 0.025%.

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The slope of any one of these lines (e.g. lanthanum) can be related to the heat effect associated with the transfer of one gram-atom of plutonium from neutron-irradiated uranium to lanthanum, or, the sum of a total or integral heat of solution of plutonium in lanthanum and a heat of dilution of plutonium in uranium, i.e.

$$\Delta H_{tr} = \underset{\text{Pu in La}}{\Delta H_S} + \underset{\text{Pu in U}}{\Delta H_D} .$$

Independent measurements of the volatilization of plutonium from metallic uranium fuel (1, 3) provide evidence that, for low concentrations in the temperature range 1540–1770° C., plutonium in neutron-irradiated uranium behaves essentially as an ideal solution. If this conclusion is accepted and, also, the assumption made that ideality extends to the lower temperatures of this work, then the heat of dilution of plutonium in uranium is zero. The measured heat of transfer, therefore, gives directly a total heat of solution, per gram-atom of plutonium, of liquid plutonium in liquid lanthanum. Also, since the equilibrium plutonium concentrations in the extractant metal are less than 0.01 atomic per cent, the heat of transfer is the limiting heat of solution or $\bar{L}^\circ_{Pu}$, the limiting partial molal heat content, relative to liquid plutonium, of plutonium in liquid lanthanum (4).

The values of $\bar{L}^\circ_{Pu}$ obtained from the present work are listed in Table IV.

TABLE IV

THE LIMITING PARTIAL MOLAL HEAT CONTENT OF PLUTONIUM IN SOME RARE EARTH METALS AT 1250°C.

Metal	$\bar{L}^\circ_{Pu}$ (kcal.)
Lanthanum	2.9±0.4
Cerium	1.1±0.4
Neodymium	0.0±0.4
Misch metal	1.1±0.4

The listed error in the heat content is that introduced by the uncertainties in a single determination of K_{Pu}.

The limiting heat of solution of plutonium appears to decrease as the atomic number increases in the "cerium" group of rare earth metals. The value of $\bar{L}^\circ_{Pu}$ decreases from lanthanum to cerium and is essentially zero for neodymium. It is interesting to note that neodymium occupies, in the lanthanide series, the same position as uranium in the actinide series and both exhibit the same limiting heat of solution with respect to plutonium as solute. The misch metal preparation used in this study is about 50% cerium and possesses a value of $\bar{L}^\circ_{Pu}$ essentially the same as that of cerium. Since the extractant is mixed in this case it is not necessary that the variation of K_{Pu} with temperature satisfy a single equation (because, say, of changing composition due to distillation of one or more of the components of the mixture). However, within the precision of the data, a straight line is obtained. Thus the addition of the other

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rare earths to cerium decreases the amount of plutonium distributed to the cerium phase but does not affect the limiting heat of solution of plutonium in the phase.

The distribution of fission product cerium has been determined in some of the experiments. In this connection it has been reported that the solubility of cerium in uranium is 1.2% at 1150° C. and may increase considerably with temperature (5). If it is assumed that all the rare earths employed in this study are equivalent in their behavior toward one another and, also, in their behavior toward uranium then, at 1150° C., 98.8% of the fission product cerium should be found in the rare earth phase and 1.2% in the uranium phase. The experimental results, which are collected in Table V, show reasonable agreement with this conclusion and provide support that equilibrium was established in the experiments.

TABLE V

DISTRIBUTION OF FISSION PRODUCT CERIUM BETWEEN URANIUM AND SOME RARE EARTH METALS

Extractant	Temp. (°C.)	Fission product Ce distribution (% original)		
		Extractant	Uranium	Crucible
Lanthanum	1160	90.8	2.1	1.6
	1276	97.5	1.4	2.8
Cerium	1200	99.6	0.0	1.9
	1250	96.0	3.2	0.3
Neodymium	1200	89.7	2.2	0.4
	1300	98.4	1.6	1.2

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L-SERYLGLYCYLGLYCINE[1]

By Erich Baer, Jonas Maurukas,[2] and Donald D. Clarke

ABSTRACT

A synthesis of the hitherto unreported L-serylglycylglycine by two different methods is described. N-carbobenzoxy L-serylglycylglycine benzyl ester, an intermediate in the preparation of the tripeptide, was found to be a suitable derivative in the synthesis of L-α-phosphatidyl L-serylglycylglycine.

In previous publications from this laboratory (1–9) methods for the synthesis of choline, ethanolamine, and serine-containing glycerolphosphatides have been described. A comparison of the synthetic and naturally occurring phosphatides led to an unambiguous elucidation of the structure and configuration of several naturally occurring lecithins, cephalins, and phosphatidyl serine. The recent discovery of naturally occurring phosphatides with peptides as nitrogenous moieties (10, 11, 18, 21, 24) challenged us to attempt the synthesis of a phosphatidyl peptide. Obviously, the difficulty of preparing peptides of even moderate chain length made it imperative that in the beginning we restrict ourselves to the synthesis of a phosphatidyl peptide with a relatively simple peptide moiety. L-Serylglycylglycine was chosen as it was expected that its preparation would not offer too many difficulties and that the phosphatidyl tripeptide would exhibit some of the properties of natural phosphatidyl peptides. Serylglycylglycine, however, is not a suitable compound for phosphorylation because of the presence of a free amino and carboxyl group. Hence, the N-carbobenzoxy L-serylglycylglycine benzyl ester, in which both groups are blocked by readily removable substituents and which is a precursor in the synthesis of the tripeptide, was used. This paper describes the synthesis of L-serylglycylglycine, a tripeptide not previously reported.

The specific rotation of L-serylglycylglycine ($[\alpha]_D^{25°}$ +32.5°) was found to be higher than that of L-serylglycine ($[\alpha]_D^{25°}$ +30.5°) reported by Fruton (19) although by analogy with peptides of a similar constitution (20) the addition of a glycine moiety to L-serylglycine should have resulted in a lower rotation. Hence L-serylglycylglycine was synthesized by a second procedure. The specific rotation of the tripeptide again was found to be +32.5°. Repeated checks bore out the correctness of this value. In addition the optical activity of L-serylglycylglycine was measured at various temperatures within the range of 11°–50°. The results are recorded in Table I.

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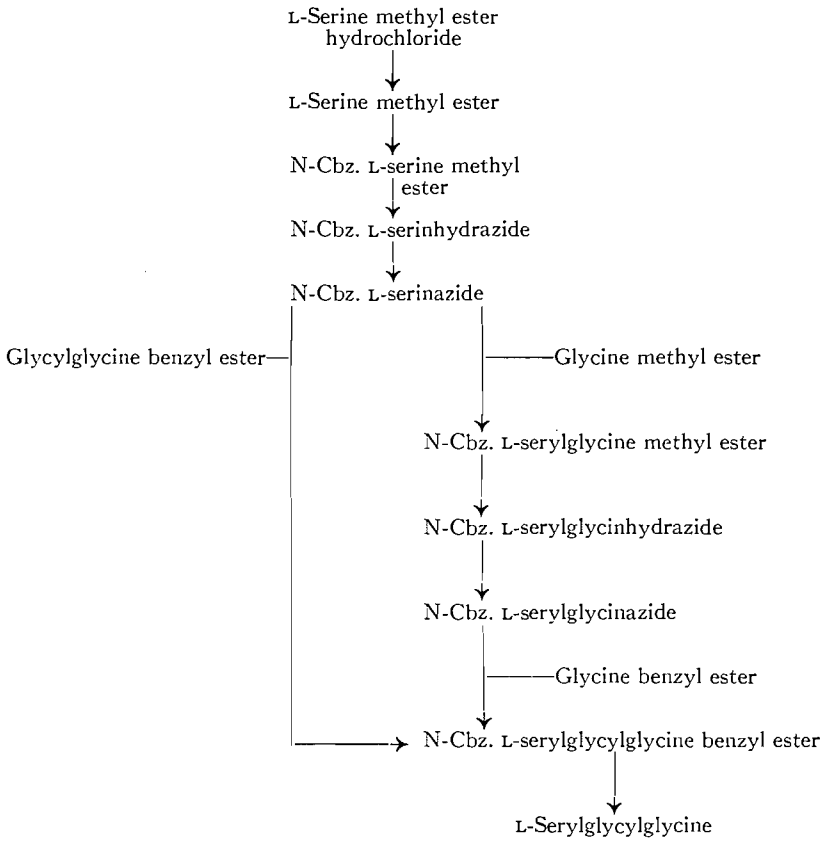
Contribution from the Banting and Best Department of Medical Research, University of Toronto, Toronto, Ontario. Supported by a Research Grant of the National Research Council of Canada, Division of Medical Research, Ottawa, Canada. An account of the work described in this paper was presented at the Symposium on Phospholipids at the University of Western Ontario, London, Ontario, Canada, October 12–13, 1955.
[2]*A section of this paper forms part of a thesis submitted by Jonas Maurukas to the Department of Pathological Chemistry of the University of Toronto in partial fulfillment of the requirements for the degree of Doctor of Philosophy.*

TABLE I

OPTICAL ROTATION OF L-SERYLGLYCYLGLYCINE AT VARIOUS TEMPERATURES

Temp. (°C.)	$[\alpha]_D$*
11	+35.4
17	+34.1
25	+32.5
30	+32.2
33	+31.6
45	+29.7
50	+28.6

Concentration: 5.4% in 1 N HCl.



Cbz. = carbobenzoxy

REACTION SCHEME

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EXPERIMENTAL

N-Carbobenzoxy L-Serylglycylglycine Benzyl Ester

Procedure I

N-Carbobenzoxy L-*Serinhydrazide*

A synthesis of N-carbobenzoxy L-serinhydrazide *via* the N-carbobenzoxy L-serine methyl ester hydrochloride has been reported by Fruton (19). Since his description is rather brief, the procedure is reported in greater detail here. *N-carbobenzoxy* L-*serine methyl ester*: In a 500 ml. two-necked round-bottomed flask equipped with a motor-driven stirrer were placed 100 ml. of water, 48 gm. of sodium bicarbonate, 75 ml. of ether, and 13.2 gm. of L-serine methyl ester hydrochloride (17). The flask was immersed in an ice-cold water bath and 10 min. later 21.0 ml. of freshly prepared carbobenzoxy chloride was added in the course of 20 min., while stirring vigorously. After two hours the bath was removed and the stirring was continued for an additional 30 min. The ether and water layers were separated, and the water layer was washed with two 35 ml. portions of ether. The combined ether solutions were freed from carbobenzoxy chloride by the addition of pyridine in just sufficient amounts to destroy the unreacted portion of the chloride, and then were washed successively with water, 2.5 *N* hydrochloric acid, and water. Drying the ether solution with anhydrous sodium sulphate and subsequent evaporation of the solvent under diminished pressure yielded N-carbobenzoxy L-serine methyl ester. (This compound was also obtained in a good yield by methylating N-carbobenzoxy L-serine (7) with diazomethane.) *Hydrazide*: The N-carbobenzoxy L-serine methyl ester, without further purification, was dissolved in 100 ml. of 99% ethanol, and to its solution was added 4.7 ml. of hydrazine hydrate. The N-carbobenzoxy L-serinhydrazide began to crystallize almost immediately. After it had been left at room temperature for 10 hr., the mixture was filtered with suction, the hydrazide was washed with cold 99% alcohol followed by ether and dried *in vacuo*. Obtained were 13 gm. of N-carbobenzoxy L-serinhydrazide (54% of the theory based on serine), m.p. 181°. Reported by Fruton (19), m.p. 181°.

N-Carbobenzoxy L-*Serinazide*

To a cold (−5°) and vigorously stirred solution of 13 gm. of N-carbobenzoxy L-serinhydrazide in a mixture of 60 ml. of glacial acetic acid and 223 ml. of 0.5 *N* hydrochloric acid was added a concentrated aqueous solution of 3.9 gm. of sodium nitrite. The azide formed immediately and precipitated as an oil. Crystallization of the azide was induced by mechanical means and the crystals were washed with ice-cold water. The dry and crystalline N-carbobenzoxy L-serinazide, which weighed 10.4 gm., and which appeared to be quite stable at room temperature, melted from 61° to 63° with the evolution of gas. On further heating the melt solidified to melt again at 169°–171°.

The higher melting substance evidently is 4-carbobenzoxyaminooxazolidone-2 (m.p. 171°), which was obtained by Fruton (19) by rearrangement of N-carbobenzoxy L-serinazide in ethyl acetate solution at 40°. When Fruton's

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procedure was repeated, 4-carbobenzoxyaminooxazolidone-2, m.p. 169°–171°, with a specific rotation of $[\alpha]_D^{25}$ −50° in ethyl acetate (*c*, 0.6), was obtained. The retention of optical activity on rearrangement is in agreement with the mechanism suggested by Kenyon and Young (22) for the Curtius rearrangement.

Glycylglycine Benzyl Ester Hydrochloride

Glycylglycine (14.4 gm.) was converted to its benzyl ester benzenesulphonate as described by Miller and Waelsch for glycine (23); 39 gm. (95%) of crude product was obtained. This material was added to 325 ml. of 99% ethanol, and dry hydrogen chloride gas was passed into the mixture with swirling until a clear solution resulted. After a few minutes crystallization set in. The mixture was cooled in an ice bath, filtered with suction, and the precipitate was washed with cold 99% ethanol followed by dry ether. On recrystallization of the crude product (15.2 gm.) from 200 ml. of hot 99% ethanol, 13.0 gm. of glycylglycine benzyl ester hydrochloride (50%) was obtained, m.p. 159°–161°C.

Glycylglycine benzyl ester hydrochloride was also prepared according to the procedure of Cook *et al.* (13, 14) for the synthesis of glycyl peptides, by coupling 2-thio-5-thiazolidone with glycine benzyl ester. The chloroform which was used by these authors was replaced by dichloromethane as this solvent facilitated the crystallization of the benzyl ester hydrochloride, m.p. 159°–160°C.

Neither of these preparations gave melting point depressions with glycylglycine benzyl ester hydrochloride prepared by the method of Zervas and Theodoropoulos (26).

Glycylglycine Benzyl Ester

Glycylglycine benzyl ester hydrochloride (13.0 gm.) suspended in 130 ml. of dry chloroform was treated with dry ammonia gas in excess and the fine precipitate of ammonium chloride was removed by filtration. The solvent was distilled off under reduced pressure to remove excess ammonia, and the glycylglycine benzyl ester was redissolved in 100 ml. of chloroform.

N-Carbobenzoxy L-*Serylglycylglycine Benzyl Ester*

The solution of glycylglycine benzyl ester in chloroform, obtained in the previous step, was added to a solution of 10.4 gm. of N-carbobenzoxy L-serinazide in 200 ml. of dry ether. A precipitate was formed immediately. The mixture, after having been kept overnight at room temperature, was cooled to −10°, filtered with suction, and the solid was washed first with dry chloroform and then with dry ether. The crude material, weighing 18 gm., on recrystallization from 100 ml. of 99% ethanol yielded 13 gm. of N-carbobenzoxy L-serylglycylglycine benzyl ester (58% based on N-carbobenzoxy L-serinhydrazide), m.p. 150°–152°. A further recrystallization from ethanol yielded a material melting from 151° to 153°. Anal. Calc. for $C_{22}H_{25}O_7N_3$ (443.45): C, 59.58; H, 5.68; N, 9.48. Found: C, 59.11; H, 5.62; N, 9.50

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Procedure II

Glycine Methyl Ester

The ester was prepared from glycine methyl ester hydrochloride by the procedure of Curtius and Goebel (15), except that a small and controlled amount of water was added to ensure a rapid reaction. The modified procedure is as follows.

A mixture of 14 gm. (111.5 mM.) of finely powdered glycine methyl ester hydrochloride, 12.9 gm. (55.7 mM.) of finely powdered silver oxide, and 85 ml. of anhydrous ether, to which 15 drops of distilled water had been added, was vigorously shaken for three hours. At the end of this period the ether was decanted and the residue was washed with three 20 ml. portions of anhydrous ether. The combined ether solutions, which contained approximately 70% of the theoretical amount of the glycine methyl ester, were dried with barium oxide. The glycine methyl ester is sufficiently stable in ether solution that, if necessary, it can be stored in this form for several days without suffering decomposition.

N-Carbobenzoxy L-*Serylglycine Methyl Ester*

This substance was prepared from N-carbobenzoxy L-serinazide and glycine methyl ester following Erlanger and Brand's procedure for the preparation of substituted glycine and alanine dipeptides (16). A dry and ice-cold solution of N-carbobenzoxy L-serinazide prepared as described above from 13.0 gm. of N-carbobenzoxy L-serinhydrazide was added to an ether solution of glycine methyl ester obtained from 14 gm. of glycine methyl ester hydrochloride. The formation of the N-carbobenzoxy L-serylglycine methyl ester took place rapidly; most of it precipitated during the first 10 min. After it had been standing for 20 hr. at room temperature and one hour at −10°, the mixture was filtered by suction, the solid was washed with cold ether and dried *in vacuo* over sodium hydroxide. The crude material, weighing 14 gm., on reprecipitation from 75 ml. of warm ethyl acetate by the addition of low-boiling petroleum ether, yielded 12.5 gm. (78.5%) of crystalline N-carbobenzoxy L-serylglycine methyl ester, m.p. 100–101°. Anal. Calc. for $C_{14}H_{18}O_6N_2$ (310.3): N, 9.03. Found: N, 9.20.

N-Carbobenzoxy L-*Serylglycinhydrazide*

The hydrazide was prepared as follows (12, 16): A solution of 11.2 gm. of N-carbobenzoxy L-serylglycine methyl ester and 4.5 ml. of hydrazine hydrate in 100 ml. of 99% ethanol was refluxed for one hour. During this time most of the hydrazide precipitated as a crystalline mass. After it had been left for 12 hr. at room temperature, the mixture was filtered by suction, the hydrazide was washed with cold 99% ethanol, followed by ether, and was dried *in vacuo* over sodium hydroxide. Yield 9.4 gm. (83.9% of theory); m.p. 186°–187°, reported m.p. 181°–182° (20). This substance is relatively stable and can be stored, if necessary, for future use. Anal. Calc. for $C_{13}H_{18}O_5N_4$ (310.31): N, 18.05. Found: N, 17.74.

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N-Carbobenzoxy L-*Serylglycylglycine Benzyl Ester*

Azide: To a clear solution of 9.5 gm. (30.6 mM.) of N-carbobenzoxy L-serylglycinhydrazide in 65 ml. of glacial acetic acid and 325 ml. of 0.5 *N* hydrochloric acid was added with shaking a concentrated aqueous solution of 2.1 gm. (31.0 mM.) of sodium nitrite, and the mixture was cooled to −5°. The N-carbobenzoxy L-serylglycinazide was extracted with two 250 ml. portions of an ice-cold mixture of ether – ethyl acetate (1:1, v/v). The combined extracts were washed with a cold and concentrated aqueous solution of bicarbonate until the washings remained alkaline to red litmus paper. The cold solution of the azide, after being dried briefly with anhydrous sodium sulphate, was added to the dry ethereal solution of glycine benzyl ester that had been prepared from 9.2 gm. of glycine benzyl ester hydrochloride by the procedure of Miller and Waelsch (23). After the solution had been left for six hours at room temperature and one hour at 0°, the crystalline material was filtered off, washed with ether, and dried over sodium hydroxide *in vacuo*. The crude product (9.5 gm.) on reprecipitation from a solution in 10 ml. of 99% ethanol by the gradual addition of ether yielded 8.5 gm. of N-carbobenzoxy L-serylglycylglycine benzyl ester (62.7% based on N-carbobenzoxy L-serylglycinhydrazide), m.p. 151°–153°.

TRIPEPTIDE

L-*Serylglycylglycine*

Two grams of N-carbobenzoxy L-serylglycylglycine benzyl ester, prepared by either one of the above procedures, was dissolved in 60 ml. of 80% acetic acid (12), and to the solution was added 0.2 gm. of palladium black (25). The mixture was shaken vigorously at room temperature in an atmosphere of pure hydrogen at an initial pressure of approximately 50 cm. of water until the consumption of hydrogen had ceased completely. The hydrogen was replaced by nitrogen, the catalyst was filtered off, and both hydrogenation vessel and catalyst were washed with distilled water. The combined filtrate and washings were evaporated to dryness under reduced pressure (bath 35°–40°). The residue was dissolved in 10 ml. of water and to the solution was added with stirring 20 ml. of 99% ethanol. After cooling to −10°, the mixture was filtered with suction and the precipitate was washed with dry ethanol. The L-serylglycylglycine, which frequently was obtained in the form of a monohydrate, after being dried *in vacuo* at 120°, weighed 0.9 gm. (91% of theory). The tripeptide, obtained from N-carbobenzoxy L-serylglycylglycine benzyl ester prepared either by procedure I or II, melted with decomposition at 216° (the capillary was placed in an oil bath at 200° and the temperature of the bath was raised 10° per min.) and had a specific rotation $[\alpha]_D^{25}$ +32.5° in 1 *N* hydrochloric acid (*c*, 5.4). Anal. Calc. for $C_7H_{13}O_5N_3$ (219.2): C, 38.35; H, 5.98; N. 19.17. Found: C, 38.24; H, 5.74; N, 18.83 (Dumas).

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LYCOPODIUM ALKALOIDS

III. FUNCTIONAL GROUPS OF SOME MINOR ALKALOIDS OF L. ANNOTINUM[1]

By G. S. Perry[2] and David B. MacLean

ABSTRACT

Four minor alkaloids of *L. annotinum* have been examined by chemical methods and infrared spectroscopy for their functional groups. Acrifoline (L.27) $C_{16}H_{23}O_2N$ has a double bond, a carbonyl group, and an hydroxyl function. Annotine (L.11) $C_{16}H_{21}O_3N$ has a double bond, a carbonyl group, an hydroxyl function, and an inert oxygen probably present in an ether linkage. Alkaloid L.12 ($C_{18}H_{25}O_3N$) is *O*-acetylacrifoline. Alkaloid L.8 ($C_{16}H_{25}O_2N$) has only been studied by infrared spectroscopy where it shows carbonyl and hydroxyl absorption. All four alkaloids therefore contain a basic tetracyclic ring system as do the majority of other lycopodium alkaloids. Annotoxine, a molecular compound of acrifoline and annotine, has been isolated from extracts of Canadian plant material.

The first detailed examination of the alkaloids of *Lycopodium annotinum* L. was carried out by Manske and Marion (6) on plant material of Canadian origin. In 1952, Bertho and Stoll (4) examined *L. annotinum* L. of German origin, and more recently Achmatowicz and Rodewald (1) have intensively investigated the *L. annotinum* L. native to Poland. The work of Bertho and Stoll indicated that the alkaloidal content of the European species differed markedly from that of Canadian origin. Of the alkaloids found by Manske and Marion, Bertho and Stoll isolated annotinine and lycopodine, but failed to find obscurine, or alkaloids L.8, L.9, L.10, L.11, and L.12. They reported, however, the presence of acrifoline, previously isolated by Manske and Marion (7) from *L. annotinum* var. *acrifolium*, and several new bases—annotoxine, $C_{31}H_{42}O_5N_2$; annotine, $C_{16}H_{23}O_4N$; a base isomeric with lycopodine, $C_{16}H_{25}ON$; and another base, not well characterized, $C_{10}H_{19(21)}ON$. Achmatowicz and Rodewald found less difference between European and Canadian *L. annotinum* L. They established that annotine was incorrectly formulated and apparently identical to alkaloid L.11. Also it was shown that annotoxine was incorrectly formulated (it should be $C_{32}H_{44}O_5N_2$) and that it was a molecular compound of acrifoline, $C_{16}H_{23}O_2N$, and L.11, $C_{16}H_{21}O_3N$. In addition, they isolated annotinine, α- and β-obscurine (8), lycopodine, a base isomeric with lycopodine, L.8, and acrifoline. Of the alkaloids reported by Manske and Marion, only L.12, L.9, and L.10 are missing. Achmatowicz and Rodewald suggested that acrifoline might have been present in either of the two L.9 fractions reported by Manske and Marion (6), and that annotoxine was not isolated from the Canadian plant because the bases were separated by fractional crystallization of the perchlorates which would break down the molecular complex.

[1]*Manuscript received May 22, 1956.*
Contribution from the Department of Chemistry, Hamilton College, McMaster University, Hamilton, Ontario. Most of this work was taken from a thesis submitted by G. S. Perry to the Faculty of Graduate Studies in partial fulfillment of the requirements for the degree of Master of Science.

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Professor Bertho (3) recently stated that his group discovered in 1953 that annotoxine was a molecular compound of acrifoline and L.11, and that annotine was actually identical to L.11 (mixed melting point with a sample from Dr. Manske). He therefore assumed that the sample which they originally ascribed as a new alkaloid was simply a hydrate of L.11.

In their study of *L. annotinum* var. *acrifolium*, Manske and Marion (7) isolated annotinine, acrifoline, lycopodine, and four new alkaloids, L.28, L.29, L.30, and L.31, but failed to find obscurine, L.8, L.9, L.10, L.11, or L.12 which they found in *L. annotinum* L. However, later work by Douglas, Lewis, and Marion (5) has shown that L.8 and L.30 were identical. It would therefore seem that the differences between the two varieties are not so great as originally suspected by Manske and Marion (7). Compounds corresponding to L.28, L.29, and L.31 have not been reported by the European workers.

In the present work we were primarily interested in the chemistry of specific alkaloids and not in their relative abundance or occurrence in the plant. However, at various times we have isolated from *L. annotinum* of undetermined variety the following alkaloids: annotinine, lycopodine, obscurine, acrifoline, L.8, L.11, and L.12. From five different batches of plant material we have isolated annotoxine, which has been shown to be a molecular compound of acrifoline and L.11. The samples of plant material were derived from three different provinces, Nova Scotia, New Brunswick, and Ontario. Manske and Marion reported L.11 as characteristic of *L. annotinum* L. and acrifoline as characteristic of *L. annotinum* var. *acrifolium*. Our isolation of both alkaloids from a single preparation suggests that both alkaloids are probably present in at least one variety and perhaps in both, but were not detected by Manske and Marion possibly because of the isolation methods employed.

The chemistry of annotinine, lycopodine, and obscurine has been studied rather extensively, but the chemistry of the other alkaloids of *L. annotinum* has been dealt with only in a cursory fashion or not at all. Bertho and Stoll (4) reported that acrifoline contained no N—CH_3, O—CH_3, or OH groups, but apparently contained a carbonyl group on the basis of its ultraviolet spectrum and its reaction with phenyl lithium. Lack of reactivity toward peracetic acid and selenium dioxide led them to propose a fully saturated ring system for the alkaloid. Acrifoline did not undergo Hofmann degradation, but phenylacrifoline did. Likewise they stated that acrifoline did not hydrogenate, but gave no experimental details. They also stated that 2,4-dinitrophenylhydrazine gave no reaction, nor did treatment of the base with benzaldehyde and sodium ethylate.

Bertho and Stoll (4) reported that annotine (L.11) had no —OH, =N—CH_3, or —OCH_3 groups. However, it reacted with phenyl lithium and lithium aluminum hydride, but their interpretation of these reactions was complicated by their misconception concerning the correct molecular formula of the alkaloid. They reported with lack of experimental detail that annotine failed to react with benzaldehyde and sodium methylate, with hydrogen, with selenium dioxide, or with hydrazine. Neither did its methiodide undergo Hofmann degradation, nor would the alkaloid react with cyanogen bromide or hydrochloric acid.

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No information on the nature of the function groups of L.8 or L.12 is recorded in the literature other than that L.8 is tertiary since it forms a methiodide on treatment with one mole of methyl iodide (1). Likewise acrifoline and annotine are tertiary bases (1).

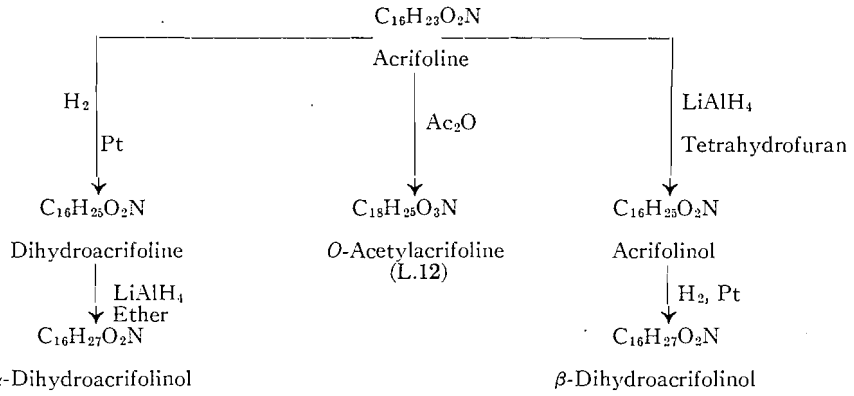
Our studies have established with reasonable certainty the nature of the functional groups in the four alkaloids, acrifoline, annotine (L.11), L.8, and L.12. Some other reactions of interest are also reported.

We have examined acrifoline by both infrared spectroscopy and chemical methods. The infrared spectrum of acrifoline in nujol showed very strong absorption in the hydroxyl region, but very weak absorption in the carbonyl region. However, in chloroform solution there was a strong band at 1700 cm.$^{-1}$ in the carbonyl region and another band at 1675 cm.$^{-1}$ which has been assigned to an unsaturated linkage. These functional groups have been confirmed by chemical treatment. Thus acrifoline underwent catalytic reduction over Adams' catalyst at 50 p.s.i.g. to give dihydroacrifoline which was analyzed as its hydrochloride and hydrobromide salts. Dihydroacrifoline was difficult to purify in a form suitable for analysis, but its infrared spectrum was examined and contained only hydroxyl and carbonyl absorption. We were unable to determine the degree of unsaturation of acrifoline in a microhydrogenation apparatus presumably because of insufficient pressure. This may explain the statement of Bertho and Stoll (4) that acrifoline failed to absorb hydrogen. Reduction of dihydroacrifoline by lithium aluminum hydride yielded α-dihydroacrifolinol, $C_{16}H_{27}O_2N$, which in its infrared spectrum contained hydroxyl but no carbonyl or double bond absorption. By hydride reduction of acrifoline in boiling tetrahydrofuran, the compound acrifolinol, $C_{16}H_{25}O_2N$, was obtained. This reduction failed to proceed in ether solution. Acrifolinol exhibited strong absorption in the infrared in the hydroxyl region, weak absorption in the unsaturation region, and no absorption in the carbonyl region. When acrifolinol was treated with hydrogen over Adams' catalyst, an isomeric β-dihydroacrifolinol, $C_{16}H_{27}O_2N$, was obtained which had an infrared spectrum similar, but not identical, to the α-compound. These two substances are undoubtedly stereoisomers; the isomerism could either be about the newly-formed hydroxyl group or about the centers of the original double bond in acrifoline.

Attempts to dehydrate acrifoline with boiling hydrochloric acid or phosphorus oxychloride led to recovery of starting material. However, treatment with acetic anhydride yielded a monoacetate, $C_{18}H_{25}O_3N$. This monoacetate melted at 119.2–120.2° C. and did not depress the melting point of a sample of alkaloid L.12, which was kindly supplied by Dr. R. H. F. Manske. The infrared spectra of the two compounds were also identical. Thus alkaloid L.12 is the *O*-acetyl derivative of acrifoline. The alkaline hydrolysis of alkaloid L.12 yielded acrifoline and thus no change in skeletal structure had occurred during the acetylation process.

The basicity constant, pK_a (pH at half titration), of acrifoline was found to be 8.34 while that of dihydroacrifoline was 9.13. The increase in basic strength on reduction can be accommodated on the basis of an allylamine structure for acrifoline. Increases of this order have been noted in similar cases (2). These results are summarized in the chart below.

REACTIONS OF ACRIFOLINE



The alkaloid annotine,[3] $C_{16}H_{21}O_3N$, has also been studied by infrared spectroscopy and chemical methods. The infrared spectrum contained a weak band in the hydroxyl region, a double peak in the carbonyl region, and weak absorption assigned to unsaturation. The presence of these functional groups has been confirmed by chemical methods.

Contrary to the report of Bertho and Stoll (4), we were unable to reduce this alkaloid by lithium aluminum hydride in either ether or tetrahydrofuran. However, it was reduced readily by sodium borohydride in ethanol to yield annotinol, $C_{16}H_{23}O_3N$. This base was crystallized from ethanol and isolated in a solvated form, but lost weight on drying corresponding to approximately two moles of ethanol. In its infrared spectrum the unsolvated base contained a double band in the hydroxyl region and weak absorption attributable to unsaturation, but no carbonyl absorption was present. Catalytic reduction of annotinol yielded dihydroannotinol, $C_{16}H_{25}O_3N$, which showed only hydroxyl absorption in the infrared region. As in the case of acrifoline, it was not possible to measure the unsaturation of annotine in a microhydrogenation apparatus. However, annotine did absorb one mole of hydrogen over Adams' catalyst at 50 p.s.i.g. to yield dihydroannotine, $C_{16}H_{23}O_3N$, which now showed hydroxyl and carbonyl absorption but no bands attributable to unsaturation.

The presence of a single carbonyl group in annotine was confirmed by its reaction with phenyl lithium to yield phenylannotine, $C_{22}H_{27}O_3N$. This compound showed no carbonyl absorption, and since only one mole of phenyl lithium had reacted, there must be present only a single carbonyl group in the alkaloid. The presence of a single hydroxyl function was demonstrated by conversion to a monoacetate which showed no hydroxyl absorption in the infrared. There was no structural change during the acetylation reaction since hydrolysis of the monoacetate regenerated annotine. The third oxygen of annotine must therefore be present as an ether.

Unlike annotinine (7), the major alkaloid of *L. annotinum*, which also contains an ether function, the ether linkage in annotine is inert. Whereas an-

[3]*We have used the name annotine in the subsequent discussion in preference to the designation L.11 and we suggest that this name should be adopted for the alkaloid.*

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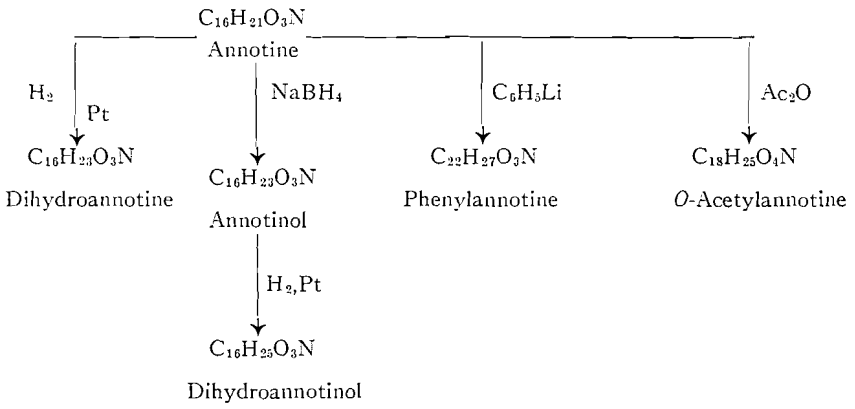
notinine forms a chlorohydrin readily by the action of concentrated aqueous hydrochloric acid, annotine does not react in a similar fashion. Instead, treatment with boiling hydrochloric acid yielded an isomeric compound, $C_{16}H_{21}O_3N$, which contained no chlorine. The substance was isolated as its hydrochloride and although its infrared spectrum was very similar to annotine hydrochloride, the carbonyl band was shifted by 10 cm.$^{-1}$ and there were distinct differences in the 600–1200 cm.$^{-1}$ region. The present state of our knowledge does not allow an interpretation of this isomerization reaction. It would seem, however, that an epoxide group is not present in the alkaloid and that the ether ring must be of a larger size.

The basicity constants of annotine and dihydroannotine were found to be 7.5 and 8.61 respectively. This increase in basic strength on reduction is similar to the case of acrifoline and a similar interpretation can be drawn. The reactions of annotine are summarized in the chart below.

REACTIONS OF ANNOTINE



The other alkaloid which we examined was alkaloid L.8, $C_{16}H_{25}O_2N$. Our investigations were limited to an examination of its infrared spectrum which showed strong carbonyl and hydroxyl absorption; thus the alkaloid most likely contains one function of each type.

With a knowledge of the functional groups of these four alkaloids and their molecular formulas, it can be calculated that they all contain a basic tetracyclic ring system. In this respect they are similar to lycopodine and (if one excludes the ether and lactone rings) annotinine as well. Therefore it seems quite likely that all of these alkaloids may have a common tetracyclic ring system and be simple derivatives of one another.

EXPERIMENTAL

Annotoxine

The mother liquors remaining after the separation of annotinine from the mixed alkaloids of *L. annotinum* were set aside in the refrigerator and after several months a crystalline material separated. The crude alkaloid obtained by filtration melted at 190–191° C. After several recrystallizations from

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acetone and methanol the compound melted at 196–197° C.[4] A mixed melting point with a sample of annotoxine provided by Professor Bertho showed no depression and their infrared spectra were identical. Calc. for $C_{32}H_{44}O_5N_2$: C, 71.61; H, 8.27; N, 5.22%. Found: C, 72.13, 72.12; H, 8.53, 8.28; N, 4.86, 4.80%. $[\alpha]_D^{19} = -187.1°$ ($c = 1\%$ chloroform). Values reported in the literature are $[\alpha]_D^{20} = -179°$ (chloroform) (3) and $[\alpha]_D^{19} = -185.6°$ (chloroform) (1).

The infrared spectrum[5] shows absorption in the hydroxyl region at 3400 cm.$^{-1}$, in the carbonyl region at 1730 cm.$^{-1}$ and 1695 cm.$^{-1}$, and a band at 1665 cm.$^{-1}$ probably representing unsaturation.

Separation of Annotoxine

(*a*) *By Chromatography.*—Annotoxine, 300 mgm., was dissolved in chloroform and adsorbed on an alumina column. The column was eluted with benzene and 10-ml. fractions were collected. Annotine passed through the column with benzene and from the combined fractions 130 mgm. of pure annotine was obtained. The column was then eluted with 2% methanol in benzene to yield first a sample of impure annotoxine (70 mgm.), m.p. 163–169° C., and then acrifoline (100 mgm.). Even after several attempts we were unable to obtain a sharp separation of the two alkaloids by this method.

(*b*) *Through the Hydrobromide Salts.*—A solution of 3 gm. of annotoxine in 100 ml. of hot acetone was made acid with 48% HBr whereupon there was immediate separation of a crystalline precipitate (1.66 gm.). Concentration of the mother liquors yielded an additional crop (0.3 gm.). The combined hydrobromides were dissolved in water, basified, and chloroform extracted. The dried chloroform extracts yielded, after evaporation of the chloroform, 1.40 gm. of acrifoline identified by its infrared spectrum and a mixed melting point with an authentic sample.

The acetone mother liquors remaining after the separation of acrifoline hydrobromide were taken to dryness. The residue was dissolved in water, basified, and chloroform extracted. The dried extracts yielded 1.5 gm. of annotine identified by its infrared spectrum and mixed melting point with an authentic sample.

Acrifoline

Acrifoline was available from annotoxine as above. It was also obtained by treatment of the crude alkaloid mixture (free of annotinine) with hydrobromic acid. Acrifoline was a pinkish-white solid which melted over a rather wide range, 99–104° C., even after several recrystallizations from ether. The mixed melting point with a sample provided by Dr. R. H. F. Manske showed no depression and the infrared spectra of the two were identical. Calc. for $C_{16}H_{23}O_2N$: C, 73.56; H, 8.81; N, 5.36%. Found: C, 73.20, 73.20; H, 9.06, 8.92; N, 5.0, 4.75%. $[\alpha]_D^{19} = -266.2°$ ($c = 1\%$ chloroform). Literature values are $[\alpha]_D^{20} = -250°$ (ethyl acetate) (3) and $[\alpha]_D^{21} = -264.8°$ (acetone) (1). $pK_a = 8.34$ (50% methanol–water).

[4]*All melting points are corrected.*

[5]*Infrared spectra were carried out in nujol mull unless otherwise specified and were determined on a Perkin-Elmer No. 21 recording spectrophotometer with a sodium chloride prism.*

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The infrared absorption spectrum in nujol showed a strong band at 3310 cm.$^{-1}$ in the hydroxyl region and extremely weak absorption at 1700 cm.$^{-1}$ and 1670 cm.$^{-1}$. However, in chloroform solution there was very strong absorption at 1700 cm.$^{-1}$ and strong absorption at 1675 cm.$^{-1}$. These two bands are assigned to a carbonyl group and an unsaturated linkage respectively.

Attempts to determine the degree of unsaturation by microhydrogenation over a palladium catalyst in glacial acetic acid were unsuccessful. Under these conditions no hydrogen absorption occurred.

Annotine (L.11)

This alkaloid has so far been obtained only by the breakdown of annotoxine. After the alkaloid was recrystallized from methanol it melted at 174–176° C. A mixed melting point with a sample kindly provided by Dr. R. H. F. Manske showed no depression. Also the infrared spectra of the two samples were identical. $pK_a = 7.50$ (50% methanol–water), $[\alpha]_D^{19} = -114.5°$ ($c = 1\%$ $CHCl_3$). Literature values are $[\alpha]_D^{21} = -114°$ (chloroform) (3) and $[\alpha]_D^{24} = -110.3°$ (acetone) (1).

The infrared spectrum in nujol shows weak absorption at 3300 cm.$^{-1}$ in the hydroxyl region, and strong absorption at 1712 cm.$^{-1}$ and 1725 cm.$^{-1}$ in the carbonyl region; in carbon disulphide solution, strong absorption at 3550 cm.$^{-1}$ in the hydroxyl region; and in chloroform solution, strong absorption at 1720–1730 cm.$^{-1}$ in the carbonyl region, and at 1644 cm.$^{-1}$, which is tentatively assigned to unsaturation. Attempts to determine the degree of unsaturation by microhydrogenation were unsuccessful.

Alkaloid L.8

This alkaloid crystallized from an ether solution of some alkaloidal residues which had been freed of lycopodine and annotinine. It melted after several recrystallizations from ethanol at 179–181° C. The compound showed no depression in melting point on admixture with a sample kindly submitted by Dr. R. H. F. Manske. Also the infrared absorption spectra of the two were identical. Calc. for $C_{16}H_{25}O_2N$: C, 73.00; H, 9.51; N, 5.32%. Found: C, 72.60, 72.70; H, 9.36, 9.41; N, 5.40, 5.23%.

The infrared absorption spectrum shows a strong peak at 1710 cm.$^{-1}$ in the carbonyl region and at 3220 cm.$^{-1}$ in the hydroxyl region.

Attempts to prepare an acetyl derivative with pyridine – acetic anhydride have not been successful.

O-Acetylacrifoline (Alkaloid L.12)

A mixture of acrifoline (500 mgm.) and acetic anhydride (20 ml.) was refluxed for two hours. After it had been cooled, the anhydride was decomposed with ice water, the mixture basified with ammonia and extracted with chloroform. The dried extracts were concentrated and adsorbed on a column of alumina. Upon elution with chloroform a colorless band containing 250 mgm. of a white crystalline solid passed from the column. It was recrystallized from petroleum ether, m.p. 119–120° C. In admixture with an authentic sample of alkaloid L.12, $C_{18}H_{25}O_3N$, kindly given us by Dr. R. H. F. Manske, there was

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no depression in melting point. Furthermore their infrared spectra were superimposable. There were no absorption bands in the infrared characteristic of hydroxyl, but instead two new bands at 1740 cm.$^{-1}$ and 1230 cm.$^{-1}$, attributable to an acetoxy group, were present in addition to the carbonyl band at 1715 cm.$^{-1}$.

We have also isolated a small sample of L.12 directly from the plant alkaloids. *O*-Acetylacrifoline readily undergoes alkaline hydrolysis to acrifoline.

Dihydroacrifoline

Acrifoline, 300 mgm., was dissolved in 50 ml. of redistilled methanol, treated with 0.10 gm. Adams' catalyst, and subjected to a hydrogen pressure of 50 p.s.i.g. for three hours. The yellow oil remaining after filtration and concentration was dissolved in ether and filtered to free it from a little insoluble material. The concentrated ether solution deposited almost colorless crystals after it had been standing several hours in the refrigerator. Several recrystallizations from ether gave a crystalline solid melting at 162.5–169.5° C. The free base, in pure form, was difficult to obtain in good yield. Consequently the combined mother liquors were evaporated to dryness, dissolved in acetone, divided, and converted into the hydrochloride and hydrobromide salts for analysis. Both salts had melting points greater than 300° C. Calc. for $C_{16}H_{25}O_2N.HCl$: C, 64.09; H, 8.74; N, 4.67%. Found: C, 63.51, 63.48; H, 8.70, 8.71; N, 4.80, 4.85%. Calc. for $C_{16}H_{25}O_2N.HBr$: C, 55.81; H, 7.61%. Found: C, 55.50, 55.43; H, 7.46, 7.42%. The infrared spectrum of the hydrochloride contained a strong band at 3240 cm.$^{-1}$ in the hydroxyl region, and at 1704 cm.$^{-1}$ in the carbonyl region. The spectrum of the hydrobromide contained bands at 3300 cm.$^{-1}$ and 1702 cm.$^{-1}$. $pK_a = 9.13$ (hydrochloride salt and water). The infrared spectrum of the free base contained strong absorptions at 3500 cm.$^{-1}$ in the hydroxyl region, and at 1679 cm.$^{-1}$ in the carbonyl region.

α-Dihydroacrifolinol

To a solution of 100 ml. of anhydrous ether containing 10 ml. of 2.76 *M* $LiAlH_4$ in ether there was slowly added a solution of 500 mgm. of dihydroacrifoline in 50 ml. of dry ether. The mixture was stirred under reflux for eight hours. Excess $LiAlH_4$ was destroyed by careful addition of aqueous ether, the ether layer was decanted, dried over anhydrous sodium sulphate, and concentrated. The yellow residue, 400 mgm. (80% theory), melted at 195.2° C. after recrystallization from methanol–acetone. Calc. for $C_{16}H_{27}O_2N$: C, 72.40; H, 10.26; N, 5.28%. Found: C, 71.80, 72.01; H, 10.12, 10.46; N, 4.79, 4.80%. Its infrared absorption spectrum contained a strong band at 3300 cm.$^{-1}$ in the hydroxyl region, but no bands attributable to a carbonyl group or an unsaturated linkage.

Acrifolinol

Acrifoline (1.50 gm.) was dissolved in 100 ml. of tetrahydrofuran dried over sodium. To this solution there was added 5 ml. of a 2.76 *M* solution of $LiAlH_4$ in ether, and the reaction mixture was refluxed with stirring for seven hours. Excess $LiAlH_4$ was destroyed by the careful addition of moist tetrahydrofuran and the reaction mixture filtered. On contact with air it became very dark

brown in color. After concentration, the dark brown residue was dissolved in 50 ml. dilute acetic acid, basified with ammonia, and extracted several times with chloroform. The combined chloroform extracts were dried and concentrated to yield 1.2 gm. of a light green foam which recrystallized from methanol. After several recrystallizations, it yielded colorless crystals, m.p. 191.1–192.6° C. Calc. for $C_{16}H_{25}O_2N$: C, 73.10; H, 9.57; N, 5.32%. Found: C, 72.40, 72.62; H, 9.57, 9.75; N, 4.84, 4.93%. The infrared spectrum showed strong absorption at 3266 cm.$^{-1}$ in the hydroxyl region, and weak absorption at 1425 cm.$^{-1}$ attributable to unsaturation.

β-Dihydroacrifolinol

A solution of 300 mgm. of acrifolinol in 50 ml. of redistilled methanol containing 0.10 gm. of Adams' catalyst was treated with hydrogen at a pressure of 50 p.s.i.g. for three hours. The solution was then filtered free of catalyst and concentrated to yield 300 mgm. of a crystalline solid which was recrystallized from acetone–methanol. The compound melted at 165.5–167.5° C. A mixed melting point with α-dihydroacrifolinol was depressed 40 degrees. Calc. for $C_{16}H_{27}O_2N$: C, 72.40; H, 10.26; N, 5.28%. Found: C, 72.17, 72.25; H, 10.03, 10.11; N, 4.70, 4.80%. The infrared spectrum contained a strong absorption band at 3290 cm.$^{-1}$ in the hydroxyl region. The spectrum was almost identical to that of α-dihydroacrifolinol.

Annotinol

A mixture of 0.10 gm. of sodium borohydride in 20 ml. of ethanol and 500 mgm. annotine in 15 ml. ethanol was refluxed for one hour, cooled, and excess borohydride destroyed by the addition of acetic acid. Most of the alcohol was distilled off, 50 ml. of water was added, and the solution was basified with ammonia. Chloroform extraction yielded 450 mgm. of a viscous oil which crystallized after standing 18 hr. Several crystallizations from ethanol yielded a crystalline compound which softened at 113–114.5° C. but was not completely molten until 129° C. It was dried at 78° C. and 0.01 mm. Hg pressure. The compound lost 27% of its weight on drying and then melted sharply at 131.5–132.5° C. The compound $C_{16}H_{23}O_3N.2C_2H_5OH$ would show a 25% loss in weight. Calc. for $C_{16}H_{23}O_3N$: C, 69.28; H, 8.36; N, 5.06%. Found: C, 69.34, 69.25; H, 8.17, 8.20; N, 5.45%.

In its infrared absorption spectrum the base contained a broad band in the hydroxyl region at 3550 cm.$^{-1}$, and weak bands at 1650 cm.$^{-1}$ and 1403 cm.$^{-1}$ attributable to unsaturation. In carbon disulphide solution there were two bands in the hydroxyl region at 3510 cm.$^{-1}$ (strong) and 3380 cm.$^{-1}$ (broad). There was also a band at 3022 cm.$^{-1}$ attributable to unsaturation.

Dihydroannotine

A solution of 100 mgm. annotine in 50 ml. of redistilled methanol containing 50 mgm. of Adams' catalyst was subjected to a hydrogen pressure of 50 p.s.i.g. for three hours. The solution was filtered free of catalyst and concentrated to yield 100 mgm. of product which crystallized immediately on contact with ether. Several recrystallizations from methanol yielded small white crystals of dihydroannotine, m.p. 201.5–202.5° C. Calc. for $C_{16}H_{23}O_3N$: C, 69.28; H, 8.36;

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N, 5.06%. Found: C, 69.48, 69.33; H, 8.12, 8.20; N, 4.95%. $pK_a = 8.61$ (methanol). The infrared absorption spectrum contained a strong band at 3200 cm.$^{-1}$ in the hydroxyl region, and at 1728 cm.$^{-1}$ in the carbonyl region.

Dihydroannotinol

A solution of 300 mgm. of annotinol in 50 ml. of redistilled methanol containing 20 mgm. of Adams' catalyst was treated with hydrogen at 50 p.s.i.g. for three hours. The solution was filtered free of catalyst and evaporated to dryness to yield 300 mgm. of a brown viscous oil which crystallized immediately on contact with ether. After several recrystallizations from methanol, the compound melted at 185.8° C. Calc. for $C_{16}H_{25}O_3N$: C, 68.78; H, 9.02; N, 5.01%. Found: C, 68.35, 68.35; H, 9.07, 8.95; N, 4.82, 5.08%. The infrared absorption spectrum in carbon disulphide solution contained bands in the hydroxyl region at 3500 cm.$^{-1}$ (strong), and a broad band at 3290 cm.$^{-1}$.

O-Acetylannotine

A mixture of 15 ml. of acetic anhydride and 450 mgm. of annotine solution was heated under reflux for 30 min. The reaction mixture of this stage had become very dark. Excess acetic anhydride was decomposed by shaking with ice water, the solution basified with 20% sodium hydroxide solution and then extracted with chloroform until the extracts were colorless. The dried extract was concentrated and adsorbed on a column of alumina and eluted with chloroform. A colorless band rapidly passed through the column from which about 120 mgm. of a crystalline compound was obtained. After recrystallization from methanol it melted at 180.7–182.2° C. Calc. for $C_{18}H_{23}O_4N$: acetyl (1), 13.56%. Found: acetyl, 12.00, 12.65%. The infrared absorption spectrum showed strong bands at 1732 cm.$^{-1}$ and 1250 cm.$^{-1}$ attributable to the acetoxy group, and a band at 1715 cm.$^{-1}$ due to the carbonyl group.

Alkaline hydrolysis of the acetoxy compound above yielded annotine.

Phenylannotine

Phenyl lithium was prepared from 0.35 gm. lithium and 3.7 gm. of bromobenzene in 30 ml. of anhydrous ether. To the solution of phenyl lithium there was slowly added a solution of 900 mgm. of annotine in 100 ml. ether–benzene. During the addition a white complex separated out. The reaction mixture was refluxed for one hour following the addition of the annotine, then cooled and decomposed by pouring it onto ice containing glacial acetic acid. The organic layer was separated and the acid aqueous solution washed once with 50 ml. ether. The aqueous solution was then basified with 20% sodium hydroxide solution whereupon a white precipitate formed which was extracted with chloroform. The combined chloroform extracts were dried and concentrated to yield 1.30 gm. (93% theory) of a white crystalline product. The compound was refluxed with 250 ml. of acetone until dissolved, then concentrated to about 50 ml. and set aside to crystallize. The crystalline compound obtained softened at 130° C., but it was not completely molten until 213–214° C. It was crystallized again from acetone, but without change in the melting point. Upon drying under vacuum the compound lost 24% of its weight. The formula $C_{22}H_{27}O_3N.2CH_3COCH_3$ would accommodate a 24.7% loss in weight. The infrared spectrum of the undried compound contained very strong absorption

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in the carbonyl region at 1710 cm.$^{-1}$. A sample was recrystallized from methanol to yield a product which melted, after drying under vacuum, at 214° C. In the infrared it contained no bands in the carbonyl region. The product first obtained from methanol was solvated since it lost 27.6% of its weight on drying corresponding to solvation by four moles of methanol. Calc. for $C_{22}H_{27}O_3N$: C, 74.75; H, 7.70%. Found: C, 74.30, 74.32; H, 7.70, 7.69%. In its infrared spectrum the dry material contained no bands in the carbonyl region. There was a strong band in the hydroxyl region at 3470 cm.$^{-1}$, and a weak band at 1640 cm.$^{-1}$ attributable to non-benzenoid unsaturation. There were strong bands in the 600–1200 cm.$^{-1}$ region attributable to a benzene ring.

Treatment of Annotine with Hydrochloric Acid

Annotine, 250 mgm., was refluxed for two hours with 20 ml. of 6 *M* hydrochloric acid. The acid solution was allowed to cool to room temperature, basified with ammonia, and then extracted several times with chloroform. The combined chloroform extracts were dried over sodium sulphate, and concentrated to yield 200 mgm. of a viscous brown residue which could not be induced to crystallize and gave a negative test for halogen (Beilstein test). Its infrared absorption spectrum contained bands at 3400 cm.$^{-1}$, 1735 cm.$^{-1}$, and 1662 cm.$^{-1}$, tentatively assigned to hydroxyl, carbonyl, and unsaturation respectively. The residue yielded a crystalline hydrochloride, which melted at a temperature greater than 300° C. Calc. for $C_{16}H_{21}O_3N.HCl$: C, 61.64; H, 7.07; N, 4.50%. Found: C, 61.62, 61.36; H, 6.91, 6.98; N, 4.24%. The infrared absorption spectrum of the hydrochloride contained a strong band at 3220 cm.$^{-1}$ in the hydroxyl region, a strong band at 1740 cm.$^{-1}$ with a shoulder at 1695 cm.$^{-1}$ in the carbonyl region, and weak absorption at 1420 cm.$^{-1}$ which is probably unsaturation.

A sample of annotine hydrochloride was prepared for comparison. It also melted above 300° C. Its infrared spectrum differed somewhat from that above. It contained a strong band at 3220 cm.$^{-1}$ in the hydroxyl region and strong carbonyl absorption at 1731 cm.$^{-1}$ with a shoulder at 1703 cm.$^{-1}$, but no band was detected in the 1400 cm.$^{-1}$ region. In the 600–1200 cm.$^{-1}$ region there were distinct differences between the two compounds.

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FURTHER OBSERVATIONS ON THE LEAD TETRAACETATE OXIDATION OF REDUCING DISACCHARIDES[1]

By A. J. Charlson[2] and A. S. Perlin

ABSTRACT

Evidence is presented which supports an earlier suggestion that the linkage-position in a reducing disaccharide may be determined readily by lead tetraacetate oxidation. Compounds examined include aldose and ketose disaccharides and aldobiuronic acids. Two types of reaction—one catalyzed by potassium acetate and the other non-catalyzed—are employed jointly to illustrate oxidation patterns which clearly differentiate each position of the biose linkage. Partial degradation of reducing disaccharides by lead tetraacetate oxidation is illustrated by the preparation of 2-*O*-α- and 2-*O*-β-D-glucopyranosyl-D-erythritol and 4-*O*-β-D-galactopyranosyl-D-erythritol. In turn, 2-*O*-β-D-glucopyranosyl-D-erythritol is degraded to 2-*O*-β-D-glucopyranosyl-glycerol.

A previous publication (16) described some oxidations of reducing disaccharides by lead tetraacetate. The reactions were carried out in aqueous acetic acid (2) using potassium acetate, which promoted catalysis of the carbohydrate oxidations and also permitted estimation of the formic acid released (15). Each position of the biose linkage was found to be associated with a distinctive oxidation pattern which readily differentiated it from other possible positions. It was therefore suggested that lead tetraacetate oxidation might be useful for determining the position of the linkage in a reducing disaccharide. The study has now been extended to include additional reducing disaccharides and some aldobiuronic acids which recently have become available to us. Other aspects of the lead tetraacetate oxidation of bioses are also considered in the light of recent findings with the normal (non-catalyzed) oxidation of monosaccharides (17).

The current results on structure determination are consistent with those obtained earlier (16), and the linkage-position determined for each compound is the same as that assigned by other investigators through the use of accepted methods. The data are summarized in Fig. 1 and Table I. As found previously, 1,6-aldohexopyranose disaccharides are degraded to a much greater extent than other linkage types, yielding about five moles of formic acid and consuming about six moles of oxidant. In contrast, 1,3- and 1,4-disaccharides yield little more than one mole of formic acid, most of which appears to be derived slowly from the non-reducing end-units. The latter two linkage types, however, are clearly distinguishable from each other in that the reducing end-unit of the former is cleaved only at the 1,2-hemiacetal glycol group to yield a pentose (monoformate), whereas that of the 1,4-compound is oxidized additionally at the 2,3-glycol group to give a tetrose (diformate).

These data are paralleled by results obtained from the structurally related 3-, 4-, and 6-mono-*O*-methyl-D-glucoses, allowance being made for the absence

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of a glycosidic non-reducing end-unit, which are virtually identical with the results reported previously for mono-*O*-methyl-D-galactoses. The behavior of 2-*O*-methyl sugars suggests that a disaccharide possessing a 1,2-linkage should be unique in readily yielding a mole of formaldehyde, since the primary alcohol group of the reducing end-unit would not be protected from oxidation either by the presence of a glycosidic linkage or by a formate ester group. This expectation has now been confirmed by lead tetraacetate oxidation of a known 1,2-disaccharide (7).

Two compounds, 4-*O*-β-D-mannopyranosyl-D-glucose and 4-*O*-β-D-mannopyranosyl-D-mannose, exhibit the only instances encountered of oxidation behavior which differs significantly from that expected. The reducing end-units of other 1,4-disaccharides examined—maltose, lactose, cellobiose, and 4-*O*-α-D-glucopyranosyl-D-mannose—are found to consume approximately two moles of oxidant within the first 15 min. reaction time (Table I and Ref. 16, Table I). This value, which is consistent with production of a tetrose from the reducing end-unit, is obtained by subtracting from the total consumption the quantity of lead tetraacetate consumed by the appropriate methyl monose glycoside. The latter quantity is assumed to approximate to the consumption of oxidant by the non-reducing end-unit. On the same basis, the reducing end-units of the mannosido-mannose and mannosido-glucose are found to consume only about one mole of oxidant, which corresponds to production of a pentose unit rather than the tetrose actually found. All other data (Fig. 1 and Table I), moreover, clearly indicate that the compounds should be assigned, correctly, a 1,4-linkage. In contrast, the reducing end-units of 3- and 6-*O*-α-D-mannopyranosyl-D-mannose are found to consume the predicted one mole and three moles of lead tetraacetate, respectively, by assuming that the α-mannopyranose non-reducing end-units are oxidized at the same rate as is methyl α-D-mannopyranoside. Since methyl α- and β-D-mannopyranosides are oxidized rapidly at about the same rate, the β-mannopyranose units of the two 1,4-disaccharides appear to possess an unusual ring conformation in solution, which is not easily attacked by lead tetraacetate.

The 1,4-ketohexose disaccharides, maltulose and lactulose, each liberate one mole of formic acid and consume three moles of lead tetraacetate. These results are consistent with those obtained with the aldose disaccharides and with the fact that ketose sugars yield esters of glycolic acid (17). Accordingly, the reducing end-units apparently consume only one mole of oxidant and are degraded to a glycolate ester of D-erythrose, and the non-reducing end-units yield formic acid at rates characteristic of other glucosides or galactosides. The 1,3-ketose disaccharide, turanose, shows behavior similar to that of the 2-substituted aldoses, being overoxidized by lead tetraacetate and yielding a mole of formaldehyde. These ketose disaccharides are thus comparable to aldose disaccharides in which the reducing end-unit is a pentose (compare 3-*O*-D-glucopyranosyl-D-arabinose with maltulose), differing in that the ester formed by cleavage of the hemiacetal glycol group is a glycolate, rather than a formate, ester.

Since the oxidation characteristics which distinguish a given linkage position

TABLE I

LEAD TETRAACETATE OXIDATION OF REDUCING DISACCHARIDES

Compound	$Pb(OAc)_4$ consumed[1]		Oxidation products		
	Total[2]	Reducing end[3]	Pentose[4]	Tetrose	Formaldehyde[4]
3-*O*-α-D-Mannopyranosyl-D-mannose	—	0.9,	Arabinose (1.0)	0	—
3-*O*-α-D-Glucopyranosyl-D-glucose	—		Arabinose (0.8)	0	—
3-*O*-Methyl-D-glucose	1.1	1.0	—	—	—
4-*O*-β-D-Mannopyranosyl-D-mannose	4.3	1.2	0	Erythrose	0
4-*O*-β-D-Mannopyranosyl-D-glucose	4.1	1.1	0	Erythrose	0
4-*O*-β-D-Glucopyranosyl-D-mannose	4.1	2.2	0	Erythrose	0
4-*O*-β-D-Glucopyranosyl-D-glucose	4.0	2.1	0	Erythrose	0
4-*O*-D-Glucuronopyranosyl-D-galactose	4.9	—	0	Threose	Trace
4-*O*-(4-*O*-Methyl-D-glucuronopyranosyl)-D-galactose	2.7	—	0	Threose	Trace
4-*O*-Methyl-D-glucose	2.0	—	—	—	0
6-*O*-β-D-Glucopyranosyl-D-glucose	5.7	—	—	—	—
6-*O*-α-D-Mannopyranosyl-D-mannose	6.4	3.2	—	—	—
6-*O*-Methyl-D-glucose	4.3	3.0	—	—	—
2-*O*-Methyl-D-glucose	5.0	—	—	—	1.0
3-*O*-α-D-Glucopyranosyl-D-fructose	6.1	—	—	—	1.1
4-*O*-β-D-Galactopyranosyl-D-fructose	3.0	—	0	Erythrose	—
4-*O*-α-D-Glucopyranosyl-D-fructose	3.0	—	0	Erythrose	—
3-*O*-α-D-Glucopyranosyl-D-arabinose	3.2	—	0	Erythrose	—

[1]*Corrected by the amount consumed in oxidation of formic acid to* CO_2.
[2]*Five hours' reaction time.*
[3]*Fifteen minutes' reaction time; total consumption less the consumption by the corresponding methyl glycoside.*
[4]*Moles per mole.*

are associated chiefly with the reducing end of the disaccharide, the reactions described should also be of use with aldobiuronic acids, in which the non-reducing end-units are easily overoxidized by glycol-cleavage agents owing to the formation of an intermediate active methylene group (12). Thus, the oxidation of 6-*O*-β-D-glucuronopyranosyl-D-galactose at the outset resembles that of the 1,6-hexose disaccharides (Fig. 1), despite an eventual pronounced overoxidation. Paralleling the low acid yield from 1,4-hexose disaccharides, 4-*O*-D-glucuronopyranosyl-D-galactose gives much less acid than the 1,6-compound. Oxidation of the methoxyaldobiuronic acid, 4-*O*-(4-*O*-methyl-D-

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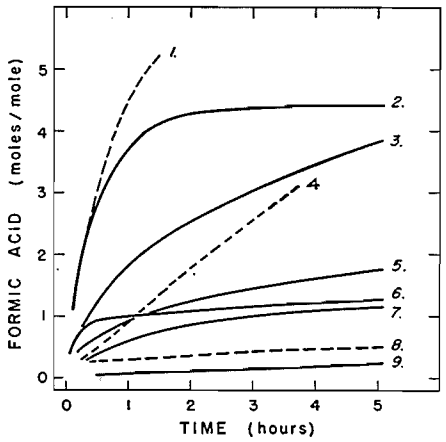

FIG. 1. Production of formic acid (evolution of carbon dioxide) during the lead tetraacetate oxidation of reducing disaccharides and aldobiuronic acids. (Compounds grouped together give identical or approximately the same rate curve; the data shown are for the first-named compound.)

1. 6-*O*-D-Glucuronopyranosyl-D-galactose
2. 6-*O*-α-D-Mannopyranosyl-D-mannose
   6-*O*-β-D-Glucopyranosyl-D-glucose
3. 3-*O*-α-D-Glucopyranosyl-D-fructose
4. 4-*O*-D-Glucuronopyranosyl-D-galactose
5. 3-*O*-D-Mannopyranosyl-D-mannose
6. 4-*O*-β-D-Galactopyranosyl-D-fructose
7. 4-*O*-D-Mannopyranosyl-D-glucose
   4-*O*-D-Mannopyranosyl-D-mannose
   4-*O*-β-D-Glucopyranosyl-D-mannose
   3-*O*-α-D-Glucopyranosyl-D-arabinose
   4-*O*-α-D-Glucopyranosyl-D-fructose
8. 4-*O*-(4-*O*-Methyl-D-glucuronopyranosyl)-D-galactose
9. 4-*O*-Methyl-D-glucose

glucuronopyranosyl)-D-galactose, illustrates more clearly the behavior of the reducing end-unit since the non-reducing end-unit of this compound does not yield formic acid and is not prone to overoxidation. Thus the formic acid production is only slightly greater than that from 4-*O*-methyl monoses, but the three moles of oxidant consumed correspond to formation of a tetrose diformate at the reducing end and cleavage of the 2,3-glycol group of the non-reducing end-unit. In agreement with these data, both 1,4-compounds yield threose (identified chromatographically) after oxidation and hydrolysis. A 1,3-linked aldobiuronic acid would be expected, accordingly, to yield one mole of pentose, and a 1,2-compound to give a mole of formaldehyde. The assignment of linkage position in aldobiuronic acids may be facilitated further by use of the oxidizing conditions considered below, in which complications due to overoxidation of the non-reducing end-unit are eliminated.

Studies on the reactions of monoses with lead tetraacetate have shown that aldoses and ketoses are degraded in a stepwise fashion, being attacked first at the hemiacetal glycol group (17). Since the rates of reaction of these compounds relative to those of glycosides (9, 15) are extremely rapid, it was to be expected that the reducing end-unit of a disaccharide should be degraded selectively under similar conditions, i.e., without potassium acetate and in the presence of only 1 to 2% of water. The rates of oxidation given in Fig. 2 are in agreement with this expectation. Aldose disaccharides possessing a 1,3-linkage quickly consume one mole of oxidant and further reaction is slow; the related 1,4-ketoses also consume one mole of oxidant rapidly. The aldose

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unit of a 1,6-compound behaves similarly to an unsubstituted aldose, rapidly taking up two moles of lead tetraacetate. In contrast, aldohexopyranose disaccharides or aldobiuronic acids having 1,4-linkages are oxidized more slowly, possibly because they are unable to assume furanose ring forms (17), glucose units being less readily attacked than galactose units. The data obtained with the corresponding monomethyl aldohexoses are virtually identical, clearly indicating that the non-reducing end-units of the bioses are not attacked appreciably during the reaction period studied. This latter point is pertinent particularly for locating the linkage in aldobiuronic acids which, as noted above, may be overoxidized in the catalyzed reaction. Since the hemiacetal group of the 2-substituted sugars is blocked, these compounds are oxidized by lead tetraacetate at a relatively slow rate. The results therefore suggest that the non-catalyzed lead tetraacetate reaction may provide useful information, complementary to that obtained with the catalyzed reaction, for differentiating the various linkage types in disaccharides and aldobiuronic acids.

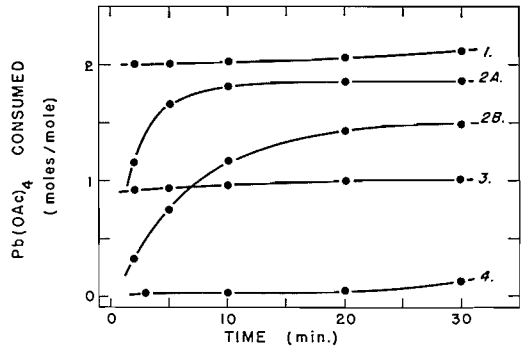

FIG. 2. Rates of lead tetraacetate consumption for reducing disaccharides, aldobiuronic acids, and mono-*O*-methyl hexoses. (Compounds grouped together give identical or approximately the same rate curve; the data shown are for the first-named compound.)

1. 6-*O*-D-Glucuronopyranosyl-D-galactose
6-*O*-D-Galactopyranosyl-D-glucose
6-*O*-Methyl-D-glucose
2A. 4-*O*-D-Glucuronopyranosyl-D-galactose
4-*O*-(4-*O*-Methyl-D-glucuronopyranosyl)-D-galactose
4-*O*-Methyl-D-galactose
2B. 4-*O*-α-D-Glucopyranosyl-D-glucose
4-*O*-Methyl-D-glucose
3. 3-*O*-α-D-Glucopyranosyl-D-arabinose
3-*O*-D-Mannopyranosyl-D-mannose
3-*O*-β-D-Glucopyranosyl-D-glucose
3-*O*-α-D-Glucopyranosyl-D-glucose
3-*O*-D-Galactopyranosyl-D-galactose
4-*O*-β-D-Galactopyranosyl-D-fructose
3-*O*-Methyl-D-glucose
4. 2-*O*-Methyl-D-glucose
2-*O*-Methyl-D-galactose

In addition to its value for the determination of structure, lead tetraacetate oxidation may be employed also for the preparation of some disaccharides by stepwise degradation of other disaccharides, in a manner already demonstrated with monosaccharides (17). To illustrate these possibilities melibiose, maltose, and cellobiose have been oxidized to give in high yields 4-*O*-α-D-galactopyranosyl-D-erythrose, and 2-*O*-α- and 2-*O*-β-D-glucopyranosyl-D-erythrose, respectively. The disaccharides were characterized as the crystalline glycosyl-erythritols. These reactions are equivalent to two successive single degradations by other procedures for descending the sugar series (6). Another possibility examined

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was that of effecting a further controlled degradation starting from the glycosyl-erythritol. For the latter purpose, the fact that a polyol is more rapidly oxidized than a glycoside (8, 9) was utilized to degrade 2-*O*-β-D-glucopyranosyl-D-erythritol to 2-*O*-β-D-glucopyranosyl-L-glyceraldehyde which was reduced in turn, affording the known 2-*O*-β-D-glucopyranosyl-glycerol. This compound has been synthesized by Carter (4) from the intermediate formed by the Koenigs–Knorr reaction using tetraacetyl glucosyl bromide and 1,3-*O*-benzylidene-glycerol. The reaction sequence described therefore provides a possible synthetic pathway for glycosyl-erythritols and -glycerols, some of which are of natural occurrence (3, 13, 18) and, as noted elsewhere (5), may afford a definitive method for determining the configuration of the biose linkage in reducing disaccharides.

EXPERIMENTAL

The following compounds were obtained from the sources indicated in brackets: 3- and 6-*O*-α-D-mannopyranosyl-D-mannose (Prof. J. K. N. Jones); the barium salt of 4-*O*-(4-*O*-methyl-D-glucuronopyranosyl)-D-galactose (Dr. J. R. Nunn); nigerose (Dr. J. H. Pazur); 4-*O*-β-D-glucopyranosyl-D-mannose and 4-*O*-β-D-mannopyranosyl-D-glucose (Prof. F. Smith); the barium salt of 4-*O*-D-glucuronopyranosyl-D-galactose (Dr. A. M. Stephen); 4-*O*-β-D-mannopyranosyl-D-mannose (Prof. R. L. Whistler).

Other compounds were prepared by methods chosen from the literature or were obtained commercially.

The procedures used for determination of formic acid, lead tetraacetate consumption, pentose, and formaldehyde have been described previously (16).

Paper chromatography of the alcohols obtained from the degradation of disaccharides was carried out on Whatman No. 1 filter paper using butanol–ethanol–water (40: 11: 19 v/v) (11) as solvent and ammoniacal silver nitrate as spray reagent (14). The term R_{gal} denotes the rate of movement of the spots produced relative to galactose.

Solutions were concentrated at 40°C. *in vacuo*.

Examination of the Oxidation Products for Pentose or Tetrose Units

This was carried out as illustrated by the following example: 1.02 mgm. of 3-*O*-D-mannopyranosyl-D-mannose in 0.01 ml. of water was taken up in 0.1 ml. of acetic acid. Lead tetraacetate (4.0 mgm., 3 molar equivalents) in 0.4 ml. of acetic acid was added. Aliquots (0.05 ml.) of the solution were withdrawn at intervals for estimation of pentose; found: 1.06 moles (10 min.), 1.06 moles per mole (45 min.). Oxalic acid (10 mgm.) in acetic acid was added with stirring to the solution remaining, and 30 min. later the precipitate of lead oxalate was removed on the centrifuge. The acetic acid was evaporated off, the residue taken up in 0.2 ml. of water and heated in a sealed tube for three hours on the boiling water bath. The hydrolyzate, on examination by paper chromatography with various solvents, was found to contain only arabinose and mannose (aniline oxalate spray (10)) which, visually, were present in approximately equal amounts.

Measurement of Oxidation Rates in the Non-catalyzed Reaction

In a typical experiment 10 mgm. of maltose, dissolved in 0.2 ml. of water, was taken up in 10 ml. of acetic acid. Lead tetraacetate (200 mgm.), dissolved in 10 ml. of acetic acid, was added to the sugar solution. Aliquots (2 ml.) of the reaction mixture were removed at chosen intervals for the determination of lead tetraacetate consumed. The data are presented in Fig. 2.

*4-O-α-*D*-Galactopyranosyl-*D*-erythritol*

Lead tetraacetate (4.8 gm.) was added to a vigorously stirred solution of melibiose hydrate (1.8 gm.) in acetic acid (450 ml.) containing water (8.0 ml.). After six minutes' reaction time the solution gave a negative starch–iodide test. Oxalic acid dihydrate (0.5 gm.) in acetic acid (5 ml.) was then added, stirring being continued for an additional 30 min.; the lead oxalate was filtered off and the filtrate concentrated to dryness. The residue was taken up in water (30 ml.) and the solution was filtered, shaken with Amberlite IR–120 resin, and stored at 3°C. for 18 hr. The solution was deionized with a mixed-bed resin and concentrated, yielding a sirup (1.6 gm.). The latter, which did not crystallize and which streaked heavily on a paper chromatogram, was dissolved in water (30 ml.) and treated with sodium borohydride (400 mgm.) (1, 19). The resulting solution was kept at room temperature for 12 hr., then it was acidified with acetic acid, cations were removed with Amberlite IR–120 resin, the solution was concentrated to dryness, and boric acid was removed by repeated addition and distillation of methanol. After being taken up in methanol–ethanol the reduced product crystallized (0.9 gm.) and after one recrystallization from the same solvent had m.p. 133°C. and $[\alpha]_D^{25}$ +134° (*c*, 2, water). The compound (R_{gal}, 0.83) gave galactose and erythritol on acid hydrolysis (paper chromatographic identification). Calculated for $C_{10}H_{20}O_9$: C, 42.25%; H, 7.09%. Found: C, 42.11%; H, 6.99%.

On oxidation with lead tetraacetate – potassium acetate in acetic acid the compound yielded 1.9 moles of formic acid and consumed 5.8 moles of oxidant. Calculated for 4-*O*-α-D-galactopyranosyl-D-erythritol: formic acid, 2.0; lead tetraacetate consumption, 6.0 moles.

*2-O-α-*D*-Glucopyranosyl-*D*-erythritol*

Maltose (3.4 gm.), dissolved in water (8 ml.), was taken up in acetic acid (450 ml.) and treated with lead tetraacetate (9.2 gm.) for three hours. The addition of oxalic acid (2 gm.) in acetic acid (20 ml.) destroyed the excess lead tetraacetate and precipitated most of the divalent lead ions. The product was worked up and reduced with sodium borohydride (1 gm.) as described above. Yield, 2.8 gm. (R_{gal}, 0.90). Crystallization took place in methanol–ethanol, and after recrystallization from the same solvent the product had m.p. 147°–148°C. and $[\alpha]_D$ +130° (*c*, 1.8, water). Calculated for $C_{10}H_{20}O_9$: C, 42.25%; H, 7.09%. Found: C, 42.10%; H, 7.11%.

The compound (0.3 gm.) was acetylated by warming with acetic anhydride (2 ml.) and pyridine (0.8 ml.). The excess acetic anhydride was decomposed with ice water yielding a sirup which slowly crystallized. The acetate was

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recrystallized from ethanol (yield 0.4 gm.), m.p. 97–98°C., $[\alpha]_D$ +105° (*c*, 1.2, chloroform). Calculated for $C_{24}H_{34}O_{16}$: C, 49.82%; H, 5.92%; acetyl, 52.1%. Found: C, 49.74%; H, 5.98%; acetyl, 52.2%.

2-O-β-D-Glucopyranosyl-D-erythritol

Cellobiose (3.4 gm.) was oxidized with lead tetraacetate (9.2 gm.) in acetic acid (600 ml.) containing water (10 ml.) for four hours. The product was worked up and reduced by the method described previously yielding a solid product (2.7 gm.) which was recrystallized from aqueous methanol (R_{gal}, 0.90); m.p. 185°–187°C., $[\alpha]_D$ −17° (*c*, 2.0, water). Calculated for $C_{10}H_{20}O_9$: C, 42.25%; H, 7.09%. Found: C, 42.38%; H, 7.10%. Oxidation with lead tetraacetate – potassium acetate in acetic acid—found: formic acid, 1.0 mole; lead tetraacetate consumption, 3.8 moles. Calculated for $C_{10}H_{20}O_9$: formic acid, 1.0 mole; lead tetraacetate consumption, 4.0 moles.

The heptaacetate of the disaccharide was prepared by the acetic anhydride – pyridine method. After recrystallization from ethanol it had m.p. 116°C. and $[\alpha]_D$ −1.4° (*c*, 1.6, chloroform). Calculated for $C_{24}H_{34}O_{16}$: C, 49.82%; H, 5.92%; acetyl, 52.1%. Found: C, 50.04%; H, 5.98%; acetyl, 51.8%.

2-O-β-D-Glucopyranosyl-glycerol

Lead tetraacetate (0.49 gm.) was added to a vigorously stirred solution of 2-*O*-β-D-glucopyranosyl-D-erythritol (0.31 gm.) in acetic acid (60 ml.) containing water (1 ml.). The solution was stirred for six hours and the product was isolated by the procedure described above. The sirup obtained (0.27 gm.) was dissolved in water (10 ml.) and reduced with sodium borohydride (0.1 gm.). The reduced product (0.26 gm.) was crystallized from methanol–ethanol. A paper chromatogram showed a major spot (R_{gal}, 1.33) and a faint spot (R_{gal}, 0.90). On acid hydrolysis, glucose and glycerol were produced (identified by paper chromatography). After recrystallization from methanol–ethanol the material had m.p. 163°C. and $[\alpha]_D$ −30.2° (*c*, 1.2, water). Calculated for $C_9H_{18}O_8$: C, 42.52%; H, 7.14%. Found: C, 42.78%; H, 7.13%. Carter reports m.p. 165°C. and $[\alpha]_D^{20}$ −30.1° for 2-*O*-β-D-glucopyranosyl-glycerol (4).

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THE PARTIAL MOLAL VOLUMES OF IONS IN AQUEOUS SOLUTION

I. DEPENDENCE ON CHARGE AND RADIUS[1]

By A. M. Couture and K. J. Laidler

ABSTRACT

The density data for aqueous solutions of electrolytes have been analyzed, and partial molal volumes at infinite dilution have been calculated. The values are shown to be additive, and a set of volumes for individual ions has been prepared, based arbitrarily on a value of zero for the hydrogen ion. It is shown that for a given value of the charge the volumes vary linearly with the cube of the ionic crystal radii, and for a given radius vary with the first power of the charge. In the case of cations the equation obeyed is

$$\bar{V}_+ = 16+4.9r^3-20z_+$$

while for anions

$$\bar{V}_- = 4+4.9r^3-20\,|z_-|.$$

If the volume of the hydrogen ion is taken as -6 ml. instead of zero the same equation is obeyed for both cations and anions, namely

$$\bar{V}'_\pm = 16+4.9r^3-26\,|z_\pm|.$$

The empirical equations are discussed in terms of a simple model for ions in solution.

INTRODUCTION

Although the partial molal volumes of ions are of some considerable theoretical and practical interest, particularly with reference to the effects of pressure on equilibria and rates, comparatively little work has been done on them. Owen and Brinkley (12) and Fajans and Johnson (3) have collected values for certain ions, and a few others have been quoted from time to time. The significance of the values has occasionally been discussed (3), but no attempt appears to have been made to analyze the volumes with a view to seeing how they depend on the valence (z) of the ion, the crystal radius (r), and other factors.

The present investigation has been concerned with obtaining a more complete and reliable set of values for ions of various types, and of showing empirically how the volumes of monatomic ions vary with z and r. Later publications will deal with the application of the results to pressure effects on equilibria and rates (8), and to obtaining empirical relationships in the case of polyatomic ions.

ANALYSIS OF EXPERIMENTAL DATA

There exist extensive data (6, 9) for densities (d) of aqueous solutions of electrolytes, and the apparent partial molal volume ϕ_v may be calculated from such densities using the formula (12)

$$[1] \qquad \phi_v = M/d_0-1000(d-d_0)/d_0c.$$

Here d_0 is the density of pure water at the temperature in question, c the concentration in moles per liter, and M is the molecular weight of the solute. For ionic solutes the Debye–Hückel theory predicts (5) that ϕ_v should vary

[1]*Manuscript received June 1, 1956.*
Contribution from the Department of Chemistry, The University of Ottawa, Ottawa, Canada.

linearly with the square root of the concentration, and many of the results have confirmed this relationship (2, 11, 12, 13, 15; see, however, Ref. 16). The procedure for calculating the partial molal volume at infinite dilution, $\bar{V}$, is therefore to plot ϕ_v values against $\sqrt{c}$ and to extrapolate to zero $\sqrt{c}$.

Proceeding in this way the table of values shown in Table I has been built up.

TABLE I

PARTIAL MOLAL VOLUMES OF IONIC SOLUTES (ML./MOLE)

Solute	$\bar{V}_{solute}$	Solute	$\bar{V}_{solute}$
HCl	18.1*	AgF	−3.1
LiCl	17.1*	$AgNO_3$	28.3*
LiBr	24.0*	$MgCl_2$	15.3*
LiI	35.6*	$CaCl_2$	18.5*
LiOH	−6.3*	$SrCl_2$	18.0*
NaCl	16.6*	$BaCl_2$	23.9*
NaBr	23.5*	$Cd(NO_3)_2$	38.0*
NaI	35.1*	$ZnSO_4$	−7.6
NaOH	−6.8*	$Pb(NO_3)_2$	42.5
Na_2SO_4	11.5*	$FeCl_2$	13.8
KF	6.6*	$FeBr_2$	23.0
KCl	26.8*	$FeSO_4$	−11.9
KBr	33.7*	$CoCl_2$	10.8
KI	45.3*	$CoBr_2$	23.8
KOH	3.4*	$Co(NO_3)_2$	30.6
KNO_3	38.0*	$CoSO_4$	−4.2
K_2SO_4	31.9*	$NiSO_4$	−10.1
RbCl	31.8*	$Al(NO_3)_3$	43.0
RbBr	38.7*	$AlCl_3$	12.9
RbI	50.3*	$LaCl_3$	16.0*
CsCl	39.2*	$Fe(NO_3)_3$	49.7
CsBr	46.1*	$Fe(NO_3)_3$	36.5†
CsI	57.7*	$CrCl_3$(violet)	13.9
TlF	10.5	$ThCl_4$	17.8
		$Th(NO_3)_4$	62.6

Quoted by Owen and Brinkley (12).
†*From Landolt-Börnstein (9); all other values from the International Critical Tables (6).*

This table includes most of the salts for which reliable data are available and which are known to be fully ionized and unhydrolyzed in dilute solutions. Compounds of B, Be, Hg (ic), and Hg (ous), and salts such as $FeCl_3$ and $ThCl_4$, are not included because there is evidence that they are not completely ionized in solution, while the following salts are omitted because there is evidence that they do not ionize to form simple ions: Au halides, Sn (ous) and Sn (ic) halides, and Cd halides; $AuCl_3$, for example, forms ions like $[Au(OH)_4]^-$ and $[AuCl_4]^-$. No reliable data appear to be available for salts of Tl^{+++}, In^{+++}, and Ga^{+++}.

Table II demonstrates the additivity of the partial molal volumes of ions, an effect that of course simply demonstrates the fact that the volumes are the sums of contributions for the individual ions. Various procedures for splitting the values for salts into ionic contributions have been suggested (1, 3), but since none is above criticism we have preferred to use the arbitrary procedure (also employed by Owen and Brinkley (12)) of taking the value for the proton as zero. Based on this convention our set of volumes, which confirm Owen and Brinkley's values where they are given, is shown in Table III. The values for

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TABLE II

ADDITIVITY OF PARTIAL MOLAL VOLUMES OF IONS

	Cl		Br		I
Li	17.1	← 6.9 →	24.0	← 11.6 →	35.6
	↑		↑		↑
	−0.5		−0.5		−0.5
	↓		↓		↓
Na	16.6	← 6.9 →	23.5	← 11.6 →	35.1
	↑		↑		↑
	10.2		10.2		10.2
	↓		↓		↓
K	26.8	← 6.9 →	33.7	← 11.6 →	45.3

monatomic ions only are given in this table; those for other ions, together with a discussion of their significance, will be presented in a later publication. The values in Table III can readily be converted into values based on another standard; thus if the volume for the proton is actually X instead of zero, the values for cations will be raised by z_+X, where z_+ is the valence; the values for anions will similarly be lowered by $|z_-|X$, where $|z_-|$ is the absolute value of the valence of the ion (e.g. is $+2$ in the case of S^{--}).

Table III also includes the crystal radii of the ions, as given by Goldschmidt (4).

TABLE III

PARTIAL MOLAL VOLUMES OF IONS

($\bar{V}_{H^+} = 0$)

Ion	r(Å)	$\bar{V}_{ion}$ (ml./mole)	Remarks
Li^+	0.78	−1.0	From Owen and Brinkley (12)
Na^+	0.98	−1.5	From Owen and Brinkley (12)
K^+	1.33	8.7	From Owen and Brinkley (12)
Rb^+	1.49	13.7	From Owen and Brinkley (12)
Cs^+	1.65	21.1	From Owen and Brinkley (12)
Ag^+	1.13	−1.0	From Owen and Brinkley (12)
Tl^+	1.49	14.7	From TlF
H_3O^+	1.70	18.0	From Owen and Brinkley (12)
Mg^{++}	0.78	−20.9	From Owen and Brinkley (12)
Ca^{++}	1.06	−17.7	From Owen and Brinkley (12)
Sr^{++}	1.27	−18.2	From Owen and Brinkley (12)
Ba^{++}	1.43	−12.3	From Owen and Brinkley (12)
Cd^{++}	1.03	−20.6	From $Cd(NO_3)_2$
Pb^{++}	1.32	−16.1	From $Pb(NO_3)_2$
Zn^{++}	0.83	−22.1	From $ZnSO_4$
Fe^{++}	0.83	−25.3	Average from $FeCl_2$, $FeBr_2$, $FeSO_4$
Co^{++}	0.82	−24.6	Average from $CoCl_2$, $CoBr_2$, $Co(NO_3)_2$, $CaSO_4$
Ni^{++}	0.78	−24.6	From $NiSO_4$
Mn^{++}	0.80	−18.3	From $MnBr_2$
Al^{+++}	0.83	−43.1	Average from $AlCl_3$ and $Al(NO_3)_3$
La^{+++}	1.22	−38.3	From $LaCl_3$
Fe^{+++}	0.67	−44.6	From $Fe(NO_3)_3$—average of I.C.T. and L.B.
Cr^{+++}	0.65	−40.4	From $CrCl_3$(violet)
Th^{++++}	1.10	−54.6	From $ThCl_4$ and $Th(NO_3)_4$
OH^-	1.40	−5.3	From Owen and Brinkley (12)
F^-	1.33	−2.1	From Owen and Brinkley (12)
Cl^-	1.81	18.1	From Owen and Brinkley (12)
Br^-	1.96	25.0	From Owen and Brinkley (12)
I^-	2.20	36.6	From Owen and Brinkley (12)
S^{--}	1.84	−7.6	From Na_2S

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DEPENDENCE ON CHARGE AND RADIUS

It is obvious from an inspection of Table III that the charge on the ion has an important effect on its partial molal volume. For a given radius each unit of charge lowers the volume by approximately 20 ml. In order to elucidate the effects of charge and radius the procedure was to determine the effect of radius for groups of constant charge, and then to study the charge effect separately. The monatomic cations present the most complete set of data, and it was found by trial that the volumes for these vary linearly with the cube of the crystal radii, the slope of the plot of $\bar{V}_+$ against r^3 being 4.9. The same relationship was found to apply to the other classes of ions.

In order to determine the dependence on z the values of $\bar{V}_+ - 4.9r^3$ were plotted against z. The result, shown in Fig. 1, demonstrates clearly that $\bar{V}_+$

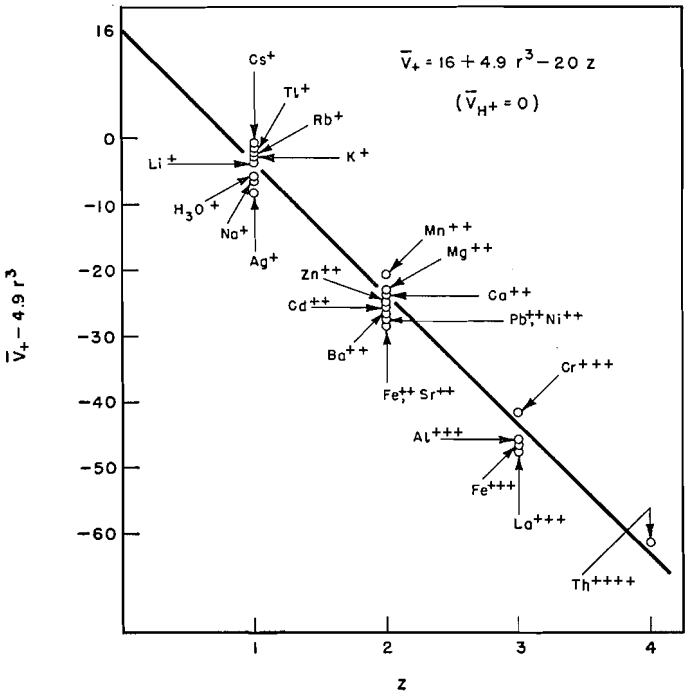

FIG. 1. Plot of $\bar{V}_+ - 4.9r^3$ against z for monatomic cations.

varies linearly with z. The intercept is 16 ml. and the slope -20, so that the empirical equation suggested by the results is

$$\bar{V}_+ = 16 + 4.9r^3 - 20z_+. \qquad [2]$$

A similar plot for the anions is shown in Fig. 2. Here the data are less extensive (there is only one point for $|z_-| = 2$) but the values are consistent with the same slope of -20, which leads to an intercept of 4. The empirical relationship obtained is thus

$$\bar{V}_- = 4 + 4.9r^3 - 20\,|z_-|\,. \qquad [3]$$

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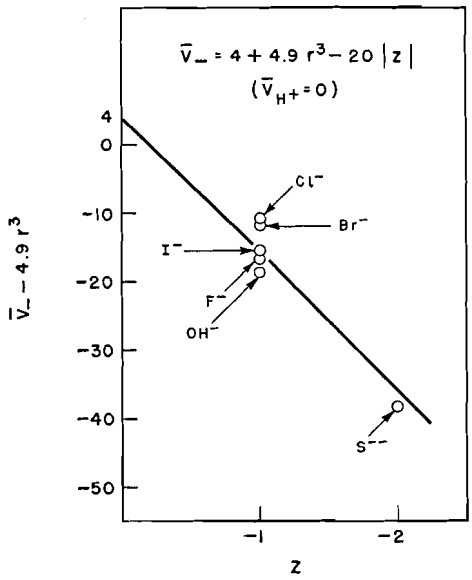

FIG. 2. Plot of $\bar{V}_- - 4.9r^3$ against z for monatomic anions.

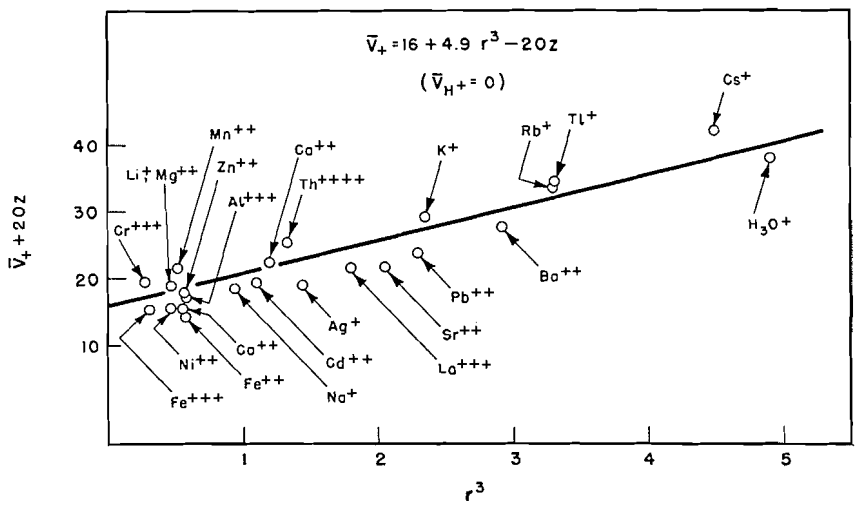

FIG. 3. Plot of $\bar{V}_+ + 20z_+$ against r^3 for monatomic cations.

The applicability of these relationships is further demonstrated in Figs. 3 and 4, which show plots of $\bar{V} + 20\,|z|$ against r^3. The linearity observed is quite satisfactory, the mean deviation of the volumes being 2.4 ml. in the case of the cations and 2.7 ml. in the case of the anions. Such deviations may be explained in part by errors in the volumes (as high as 5 ml. in the case of some of the polyvalent ions), and perhaps more importantly in terms of errors in the crystal radii. These latter errors are of course highly magnified by cubing

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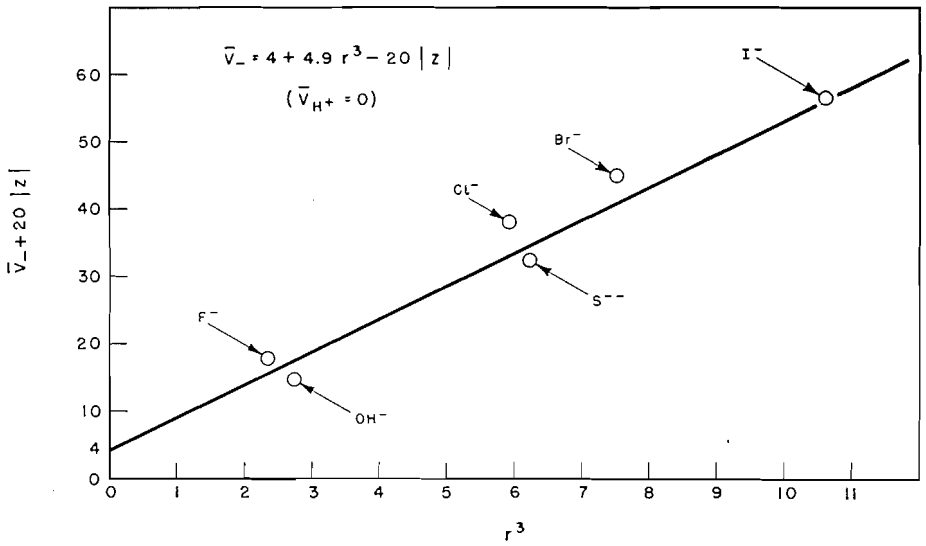

FIG. 4. Plot of $\bar{V}_- + 20\ |z_-|$ against r^3 for monatomic anions.

the radii. There are quite serious discrepancies between the crystal radii listed by Goldschmidt (4) and by Pauling (14), notably in the case of lithium for which the values are 0.78 Å and 0.60 Å respectively. In the present work the Goldschmidt values were found to give better correlations, and have therefore been used. In similar work on entropies (7) the univalent radii were found to give the best correlations, and there was little to choose between the Goldschmidt and Pauling values, presumably because $1/r$ was involved instead of r^3.

The empirical equations for cations and ions are seen to differ only in the constant term. This, however, is only a reflection of the arbitrariness in the choice of zero as the value for the proton. The two equations can be brought together if the values for all of the univalent cations are lowered by $\frac{1}{2}(16-4) = 6$ ml., and those for the univalent anions are raised by the same amount. This means that the new standard is $\bar{V}_{H^+} = -6$ ml., and accordingly the values must be lowered for all cations by $6z_+$ and raised for all anions by $6\ |z_-|$. If we define a new partial molal volume by $\bar{V}'_+ = \bar{V}_+ - 6z_+$, Equation [2] is transformed into

$$\bar{V}'_+ = 16 + 4.9r^3 - 26z_+. \qquad [4]$$

A similar procedure converts Eq. [3] into

$$\bar{V}'_- = 4 + 4.9r^3 - 14\ |z_-|\ . \qquad [5]$$

These equations are not in general identical, but become so for the particular case of $|z_-| = 1$. There is actually only one ion (S^{--}) for which $|z_-|$ is other than unity, so that with the exception of this case we may apply the general equation

$$\bar{V}'_\pm = 16 + 4.9r^3 - 26\ |z_\pm| \qquad [6]$$

to both cations and anions. Fig. 5 shows a plot of $\bar{V}'_\pm + 26\ |z_\pm|$ against r^3.

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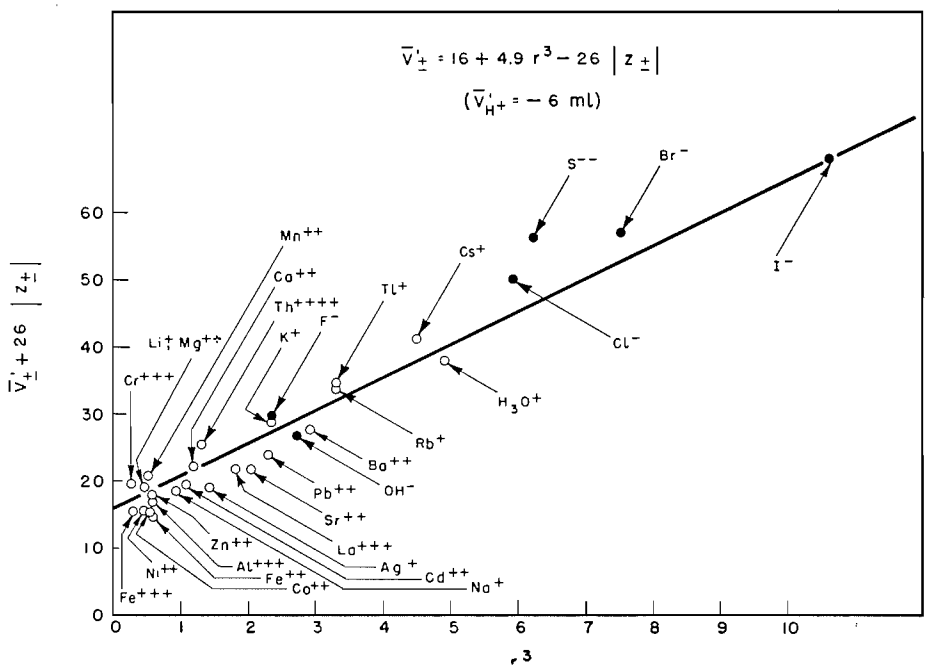

FIG. 5. Plot of $\bar{V}'_{\pm}+26\ |z_{\pm}|$ against r^3 for both monatomic cations and anions; $\bar{V}'_{\pm}$ is the partial molal volume relative to $\bar{V}_{H^+} = -6$ ml.

The correlation is satisfactory, and even the point for S^{--} is not too badly off the line. The mean deviation in this case is 2.7 ml.

DISCUSSION

The physical significance of the empirical equations that have been developed is not hard to understand. The volume occupied by an ion in aqueous solution may be considered to be made up of two terms: (1) a term related to the intrinsic volume of the ion itself, and (2) a term related to the electrostriction of water molecules in the neighborhood of the ion. On the simplest view the first of these terms would be simply $4/3.\pi r^3$, which works out to be $2.5r^3$ ml. per mole, where r is expressed in angstroms. The item that actually appears in the equations is $4.9r^3$, the numerical factor being approximately twice as great. The difference may be due to several causes. In the first place, the crystal radii are significantly smaller than the true radii of the ions owing to the distortion of the electronic orbitals in the crystal. Secondly, as indicated by the analysis of the entropies of ions (7), there is a free volume (of about 0.7 Å^3) associated with the ions in solution, and this must be added to the apparent volumes. These two factors seem to be quite sufficient to account for the apparent discrepancy between the coefficients of r^3.

In this connection it is of interest to note that Lee (10), on the basis of the partial molal volumes of uni-univalent electrolytes in aqueous solution, has proposed the equation

$$V = 1.87(V_+ + V_-) - 20.7 \quad [7]$$

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where V_+ and V_- are the volumes of the ions in the crystals. Our Equations [2] and [3] lead to

$$[8] \qquad V = \bar{V}_+ + \bar{V}_- = 20 + 4.9(r^3_+ + r^3_-) - 20(z_+ + |\, z_- \,|)\ .$$

For the special case of a uni-univalent electrolyte this equation becomes, with $V_+ = 2.5r^3_+$ and $V_- = 2.5r^3_-$,

$$[9] \qquad V = 1.96(V_+ + V_-) - 20.$$

This equation closely resembles that of Lee.

The empirical equations obtained for ionic volumes are to be contrasted with those obtained (7) for ionic entropies, where a variation with z^2/r was found. It is of particular interest that entropies depend on z^2 (as predicted by the Born equation) and volumes on z.

It may be noted in conclusion that the present treatment makes no explicit reference to ionic hydration. The electrostriction terms in the empirical equations do in a sense cover the effects of hydration, but in our view the concept of ionic hydration has not proved to be a particularly useful one. The electrical field in the neighborhood of an ion falls continuously with increasing distance, and it is therefore arbitrary to regard some of the water molecules as associated with the ion and others as not. It is no doubt for this reason that different methods of measuring ionic hydration numbers lead to such widely different results.

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THE REACTIVE COMPONENTS IN ACTIVE NITROGEN AND THE ROLE OF SPIN CONSERVATION IN ACTIVE NITROGEN REACTIONS[1]

By H. G. V. Evans[2] and C. A. Winkler

ABSTRACT

Critical examination of the available experimental information provides rather convincing evidence that atomic nitrogen is the main reactive species in active nitrogen. It appears quite unlikely that a significant contribution to the activity is made by electronically excited molecules, metastable atoms, ions, or triatomic radicals. Evidence exists, however, for the presence of more than one active species, and a plausible suggestion would seem to be that the second species is vibrationally excited molecules. Consideration of the role of spin conservation in reactions of active nitrogen leads to the conclusion that reactions that conserve spin occur more readily than those in which spin is not conserved.

INTRODUCTION

A proposed unified interpretation (15) of the many reactions of active nitrogen that have now been studied made it essential to define as clearly as possible the nature of the reactive species in active nitrogen formed in a condensed electrical discharge. Numerous investigations into the properties of active nitrogen have been made and explanations of its behavior have been suggested from time to time. However, there is no recent critical evaluation which seeks to correlate all the results. Such an evaluation seems possible, and is attempted in the present paper, now that the dissociation energy of the nitrogen molecule has been established with virtual certainty.

THE REACTIVE COMPONENTS OF ACTIVE NITROGEN

Atoms and molecules in almost every conceivable excited state have been suggested as possible active species in active nitrogen. It is now widely accepted that the activity is due mainly, though perhaps not entirely, to atomic nitrogen (8, 12, 33, 45, 52, 56).

Electronically Excited Molecules and Atoms as Active Species

The $A^3\Sigma$ state should be the longest lived electronically excited state of molecular nitrogen.[3] During the emission of the Lewis–Rayleigh afterglow of active nitrogen the $A^3\Sigma$ state is continually being formed in small amounts because it is the lower state of the electronic transition $B^3\Pi \rightarrow A^3\Sigma$ that gives the afterglow (Fig. 1[4]). It has a lifetime with respect to radiation of 10^{-3} to 10^{-4} sec. (47) and must have a still shorter lifetime with respect to collisions to explain the absence of Vegard–Kaplan bands in the emission spectrum of

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Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Quebec, with financial assistance from the National Research Council.
[2]*Holder of a National Research Council Studentship and Fellowship.*
[3]*The metastable $a^1\Pi_g$ state has also been suggested (43, 48) as a possible active species. This state is the upper state of the Lyman–Birge–Hopfield bands (Fig. 1) which appear to be more "allowed" than the "forbidden" Vegard–Kaplan bands emitted by the $A^3\Sigma$ state (27).*
[4]*Adapted from Ref. 51.*

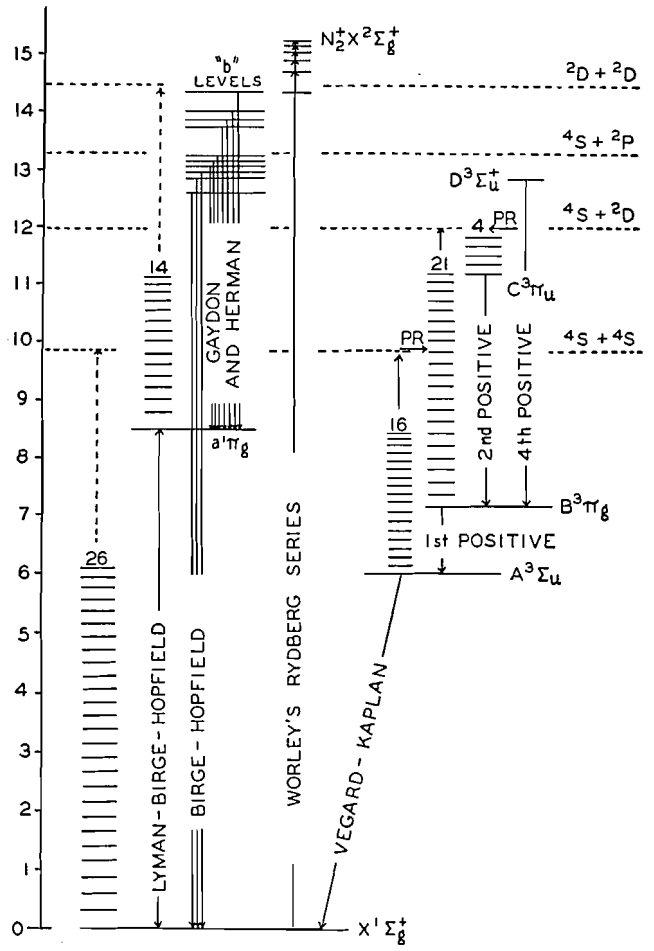

FIG. 1.

the afterglow. In the conventional fast flow systems used to study the chemical reactions of active nitrogen (e.g. 14), a lifetime of about 10^{-3} sec. for electronically excited nitrogen molecules formed in the discharge tube would mean that their concentration would be reduced by a factor of about 10^9 by the time they reached the reaction vessel. Since collisions will reduce the lifetime considerably below 10^{-3} sec., it seems quite certain that electronically excited nitrogen molecules formed in the discharge would not reach the reaction vessel in significant concentrations.

Benson (2) has suggested that emission of the afterglow occurs by metastable molecules going over into adjacent levels of the $B^3\Pi$ state (which emits the afterglow spectrum). He examined the transient response of the afterglow to the sudden increase in pressure caused by shock waves in active nitrogen and observed that the initial jump in intensity across the shock front depended on density instead of collision rate. By using interference filters, he found a marked difference in behavior of the yellow (5750±40 Å) and green (5640±

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100 Å) parts of the spectrum. To reconcile these results with other work, if the dependence on density rather than collision rate is real, it would be necessary to assume that in the emission process an intermediate state is formed from nitrogen atoms by recombination in a triple collision and that this state has a lifetime of at least 10^{-4} sec. (The time of response of the photocells was less than 10^{-4} sec., and the radiative lifetime of B molecules is only about 10^{-8} sec.). However, the main evidence for the intensity dependence comes from measurements of intensities in the green spectral region, where the behavior is not what would be expected from either the known effects of increased pressure (39, 53) or the usual intensity distribution of the afterglow spectrum (51).[5] A little oxygen present in the shock tube experiments would result in emission of the green bands of nitric oxide (51) and it is perhaps well not to draw definite conclusions until this possibility has been examined experimentally.

Under special experimental conditions it is possible to excite other afterglows in nitrogen (34, 35, 36). These afterglows, in contrast to the Lewis–Rayleigh afterglow, have very short lifetime and show time-dependent intensity distributions in their spectra, which involve excited nitrogen molecules, molecule ions, and atoms.

The spectrum of the so-called "auroral" afterglow contains the forbidden Vegard–Kaplan bands emitted by nitrogen molecules in the metastable $A\,^3\Sigma$ state and forbidden lines emitted by nitrogen atoms in the metastable ^2P state (37, 38). The Lewis–Rayleigh afterglow, on the other hand, does not show either of these spectra, which indicates that neither of these metastable species is present in significant concentration in active nitrogen prepared by the usual methods (33).

This argument does not apply to atoms in the ^2D state in which the radiative lifetime is about 10,000 times that in the ^2P state (26). The magnetic resonance spectrum of active nitrogen (24) shows atomic nitrogen in the ^4S ground state to be present, but not the metastable ^2P and ^2D states. However, there should be nothing to prevent ^2D atoms from transferring their excitation energy in collisions of the second kind with other atoms. A careful search (23) showed no evidence for such resonance transfer in the spectra of metallic vapors excited by active nitrogen in a flow system, and it is probably safe to conclude that the concentration of excited nitrogen atoms is very low.

The fact that active nitrogen shows no absorption spectra in the region 2000 to 8700 Å (6, 25) is a further strong argument against the presence of significant concentrations of electronically excited nitrogen molecules and atoms in active nitrogen. All the known excited states would show absorption in this region (Fig. 1, Ref. 51). On the other hand, the first allowed transitions for nitrogen atoms and molecules in the ground state lie in the far ultraviolet.

[5]*Benson's explanation of the selective enhancement of one part of the spectrum does not appear to be acceptable. The most intense bands in both spectral regions selected by the filters used arise from transitions from the same vibrational levels of the B state going to different levels of the A state and the relative intensities are the same (56) so that a change in population in the vibrational levels of the B state would not give an increased intensity in only one region. Benson shows a photograph of the spectrum of the afterglow in active nitrogen flowing through a nozzle at supersonic velocity. There is no indication of any change in the relative intensities of different parts of the spectrum in going from the high pressure to the low pressure side.*

Nitrogen atoms in the metastable ^2P and ^2D states, and molecules in the metastable $A\,^3\Sigma$ state, have been introduced into mechanisms for afterglow emission for two main reasons: (i) to explain the selective enhancement of certain vibrational levels in the emission of the afterglow (8, 9, 49), and (ii) to explain the excitation of 9.6 ev. emission with only 7 ev. presumed available from recombination of two atoms in the ^4S ground state (8, 9). The adoption of 9.76 ev. for $D(N_2)$[6] prevents the operation of the first of these processes (56) and removes the necessity for explaining the second. Moreover, these mechanisms cannot explain the termolecular kinetics of the decay process (39, 53, 70, 72, 73) and the observed constancy in the relative intensities of different parts of the afterglow spectrum during the decay (9).

Charged Particles as Active Species

At one time Mitra (44) suggested that the activity of active nitrogen was due to the presence of N_2^+ ions. This theory was based on analogous processes that were thought to occur in the emission of the spectrum of the night sky, and on the very large energies transferred to metal foils in some experiments made by Lord Rayleigh (54). It has since been found that the interpretation of the atmospheric spectrum in terms of N_2^+ was wrong (7) and that Rayleigh's results were due to bombardment by electrons from the exciting discharge (2). Mitra has therefore suggested recently (45) that the activity of active nitrogen is due to nitrogen atoms.

In the absence of an ion trap after the exciting discharge, streaming active nitrogen contains a very low concentration of electrons (less than one free electron for 10^6 molecules of nitrogen (2, 10)). Such a low concentration of free electrons should not affect processes occurring in the gas phase to any extent, but might affect processes on the walls of the system.

The physical properties of active nitrogen are not changed by the removal of charged particles (2, 63)[7] and it seems unlikely that charged particles have an appreciable effect on the chemical reactivity of active nitrogen.

Atoms in the ^4S Ground State as Active Species

The long life of active nitrogen (52) and its sensitivity to wall conditions (22, 55) are immediately explained if atoms are the active species, and their presence has been shown directly by the excitation of the atomic lines with an auxiliary discharge (1), by Wrede gauge measurements (75), by the magnetic resonance spectrum (24), and by the mass spectra (29). The most convincing evidence that they play the principal role in the emission of the active nitrogen Lewis–Rayleigh afterglow comes from the termolecular kinetics of the decay process (39, 53, 70, 72).

The ability of active nitrogen to take part in resonance transfers of large

[6]*It now appears that the experimental (13, 16, 22, 37, 65) and theoretical (18, 20, 40) evidence is overwhelmingly in favor of 9.76 ev. for $D(N_2)$.*

[7]*Kane and Clark (31) found that a magnetic field reduced the rate of decay of the afterglow by about 3% and concluded that ions must take a part in the emission process. In view of all the other evidence, it seems likely that their interpretation of the results was incorrect, and that the effect was due to some other cause, such as change in surface condition.*

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amounts of energy in exciting atomic and molecular spectra (30, 38, 51) was largely responsible for the original suggestion (4, 46, 57) that electronically excited molecules must be present. This is not really necessary, however, since there seems to be no reason why the inverse of a photosensitized dissociation should not occur,

$$N + N + X \rightarrow N_2 + X^*.^8$$

The potential energy surfaces are the same for the reaction in either direction, and it is probable that the critical configuration would be very similar to that for the process

$$N_2^* + X \rightarrow N_2 + X^*.$$

The recombination of hydrogen atoms can excite the sodium *D* lines, and the 2537 Å line of mercury (5), and presumably nitrogen atoms might behave the same way.

The emission of electrons from metal surfaces exposed to active nitrogen (11) is somewhat more difficult to understand, but the candoluminescence observed when various activated oxides are exposed to hydrogen atoms (58) shows that atom recombination can transfer large quanta of energy to solid surfaces.

The fact that an auxiliary mild electric discharge through active nitrogen extinguishes the afterglow and excites the fourth positive bands of molecular nitrogen (63) has been interpreted (9, 32) to mean that significant concentrations of excited nitrogen molecules in metastable states are present in active nitrogen. However, in normal nitrogen a condensed discharge is required, both to excite these bands and to form nitrogen atoms (60). Hence, these results might only indicate the similarity of the conditions prevailing in a mild discharge through active nitrogen to those in a condensed discharge through normal nitrogen, where both atoms and electrons are certainly present. Wrede found (75) direct evidence that a discharge removed atoms very readily.

It has been observed that the visible afterglow disappears in a heated section of a flow tube and reappears downstream (63), and that if the glass is heated strongly enough to give off some sodium, the "dark modification" of active nitrogen can still excite the sodium *D* lines (9, 32). This has been interpreted as evidence for the presence of two active species (9, 32, 70, 72). However, these results can be interpreted just as readily if atomic nitrogen is the only active species, since the recombination process leading to the afterglow is known to have a negative temperature coefficient (53). If the extinction of the afterglow occurs because an active species is being destroyed in the hot zone, it is difficult to understand how the afterglow can reappear downstream.

Vibrationally Excited Molecules in the Ground State as Active Species

The assumption that nitrogen atoms in the ^4S ground state are the most important active species in active nitrogen makes it possible to suggest energetically reasonable mechanisms for its chemical reactions. However, recent work in this laboratory has given evidence, discussed later, that a second species of lower reactivity than atomic nitrogen is present in active nitrogen in

[8]*The symbol * represents electronic excitation.*

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significant concentrations.[9] To explain the results it is only necessary to assume that the second species can transfer quite large amounts of energy in collisions of the second kind. The previous discussion would seem to rule out all the species hitherto suggested. The only species that might behave in this way, and should be present in significant concentrations, appears to be *vibrationally* excited nitrogen molecules.[10] None of the objections raised against electronically excited metastable states would apply to vibrationally excited molecules in the ground state.[11] It is well known that homonuclear diatomic molecules are very stable with respect to radiation of vibrational quanta (28) and that they may retain their vibrational energy over many thousands of collisions (42, 50). Molecular systems are very reluctant to transfer quanta of energy that are large compared with kT from internal degrees of freedom into translational motion. This means that when electronically excited nitrogen molecules are deactivated by collision they will go over into the adjacent upper levels of the ground state. Thus, the formation of short-lived electronically excited states by recombination of nitrogen atoms and in the parent discharge must ultimately lead to the formation of nitrogen molecules in the highest vibrational levels of the ground state.

Some idea of how fast such molecules will lose their energy may be obtained from the experimental results for the first excited vibrational state of CN. The probability of transfer of vibrational energy is mainly determined by the energy gap between successive vibrational levels. The gap between the first two levels of CN is 2024 cm.$^{-1}$, which is between 2331 and 1556 cm.$^{-1}$, the values for the first two levels and the last two observed levels of N_2 (28, Table 39). The collision yield for deactivation of the first excited vibrational level of CN is about 10^{-4} in pure cyanogen and about 10^{-5} in argon (68). For typical experimental conditions that have been used to study the reactions of active nitrogen, excited nitrogen molecules will undergo about 10^7 collisions per second, so that the rate constant for collisional deactivation should be between $k = 10^2$ sec.$^{-1}$ and $k = 10^3$ sec.$^{-1}$.[12] If it is assumed, for simplicity, that the rate of deactiva-

[9]*The possible presence of an unidentified second active species in active nitrogen has been suggested earlier (70, 71, 74). However, the amount of active species was estimated from the amount of nitric oxide decomposed in the nitric oxide – active nitrogen reaction, and the mechanism of this reaction is probably complex (59). Hence, the significance of the results is somewhat doubtful.*

[10]*Triatomic radicals (N_3) have been proposed as a possible reactive species (64, 66). The possibility that significant concentrations of these radicals (with long enough lifetime to be distinguished from N–N_2 complexes) are present in active nitrogen appears to be ruled out by the termolecular kinetics of the afterglow decay, and its long lifetime. If N_3 radicals were present, and able to react with other molecules, it seems reasonable that they would react fast with nitrogen atoms.*

[11]*The transparency of active nitrogen from 2000 Å to 8700 Å does not rule out the presence of vibrationally excited molecules in the upper vibrational levels of the ground state, even though part of the Lyman–Birge–Hopfield bands (with those levels as the lower state) do lie in this region. The Lyman–Birge–Hopfield bands result from a forbidden transition and are about 2000 times weaker than the allowed transitions of electronically excited atoms and molecules (27). Since the part of the system that extends beyond 2000 Å is still weaker than the main part of the system, only a very high concentration of vibrationally excited molecules could be detected by absorption in the region 2000 Å to 8700 Å.*

[12]*A recent study (42) has shown that in the collisional deactivation of vibrationally excited oxygen molecules, the energy is removed most readily when there is near resonance of the vibration levels of the collision partners. For deactivation of O_2 by N_2 or argon, the collision yield is less than 10^{-7}, which indicates that these estimates for k may be somewhat high.*

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tion is the same for all vibrational levels, it is possible to derive an expression (Appendix) for the fraction of molecules which have lost j quanta

$$M_{n-j}/M_n{}^0 = x^j e^{-x}/j!$$

where $M_n{}^0$ = initial concentration in the nth vibrational level,
M_{n-j} = concentration in the $(n-j)$th level,
x = kt, where k is the mean rate constant and t is the time.

Fig. 2 shows the distribution curves for three values of kt. It has been assumed that all the excited molecules were initially in the highest observed level. In the apparatus used to study reactions of active nitrogen, the time required for the gas stream to pass from the discharge tube to the reaction vessel is

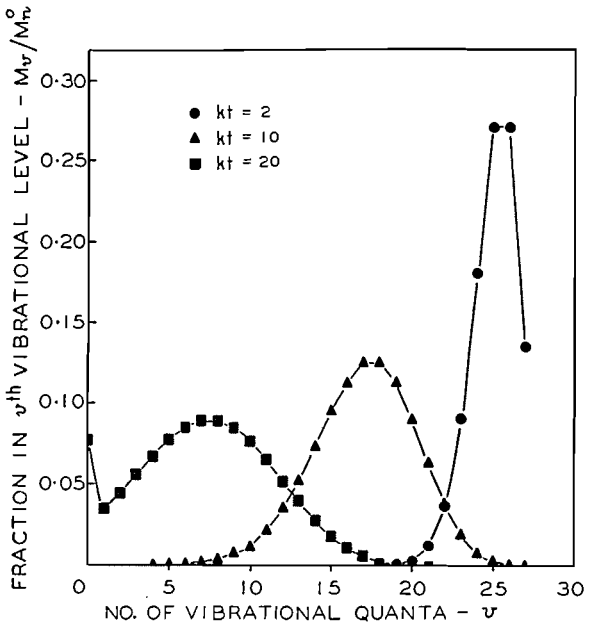

FIG. 2.

generally about 0.02 sec. Hence, the distribution curves of Fig. 2 will give the distribution of excited molecules reaching the reaction vessel for two extreme values and an average value of k. The most highly populated levels have excitation energies of about 140, 98, and 42 kcal. for kt values of 2, 10, and 20 respectively. It seems likely that these energies are, if anything, rather too low, since there must be several widely spaced levels above the highest observed level.[13]

Recently, a mass spectrometric analysis of active nitrogen has been made (29). The appearance potentials of the mass 14 and 28 peaks were compared with those from normal nitrogen. The ion current vs. electron energy

[13]*Extrapolation of the observed levels from the highest observed level (at 6.6 ev. above the zero level) to the dissociation limit at 9.76 ev. shows that the potential curve does not decrease markedly in slope until well above the last observed level (19).*

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curves from the mass 28 peaks were superimposable, but those for the mass 14 were quite different. The mass 14 curve of active nitrogen showed an inflection that indicated N^+ ions to be formed by two processes with appearance potentials of 14.7 and 16.1 ev. The first value corresponds closely to that expected for the process

$$N(^4S) + e \rightarrow N^+ + 2e$$

which provides direct evidence for the presence of ^4S atoms in active nitrogen. If the second process is

$$N_2\dagger + e \rightarrow N(S^4) + N^+ + 2e$$ [14]

with an appearance potential of 16.1 ev., $N_2\dagger$ molecules with excitation energies greater than 8 ev. must be present in active nitrogen.

While there would seem to be a good possibility for a significant concentration of molecules with more than 100 kcal. of vibrational excitation to be present in the reaction vessel, the average time spent in the reaction vessel is generally about 0.2 sec., and most of the excited molecules should have time to pass their excitation energy to other molecules. Since the principle of resonance is approximately obeyed for the transfer of vibrational energy, and the vibrational quanta of the nitrogen molecule are between 4.5 and 6.6 kcal., foreign molecules should have a good chance of acquiring 5 kcal. or more of vibrational energy. This means that the vibrational temperature in the reaction vessel might be much higher than the translational temperature, particularly since nitrogen atoms must give products with considerable vibrational energy. Thus, considerable caution must be exercised in interpreting measured activation energies.

In view of the arguments advanced above in favor of only one-quantum transfers, it may well be asked how vibrationally excited nitrogen molecules may be an active species that can transfer all, or nearly all, their excitation energy in collisions of the second kind. The answer might lie in the presence of neighboring electronically excited states (Fig. 1). Transfer from the potential curve of the ground state to the potential curve of, for example, the $A\,^3\Sigma$ state might well occur during a collision provided the internal energy were sufficient. Such a process would be the inverse of the collisional deactivation of the $A\,^3\Sigma$ state which, as indicated previously, is known to occur quite readily. Since both the nitrogen and its collision partner must be considered, the process must be described in terms of multidimensional potential energy surfaces, the resonance transfer of energy occurring by a radiationless transition from one surface to another corresponding to a different electronic configuration. This picture is essentially similar to that which has been suggested (41) to explain the chemiluminescent emission of the sodium D lines (3) produced by vibrationally excited sodium chloride molecules:

$$NaCl\dagger + Na \rightarrow Na^* + NaCl^*.$$

The presence of electronically excited states adjacent to the upper vibrational levels of the ground state of N_2 implies that the change in electronic configuration can occur without marked interaction between N_2 and the

[14] *The symbol † represents vibrational excitation.*

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collision partner. Thus, the resonance transfer process might be described somewhat schematically as follows:

(i) formation of a collision complex (on the ground state potential surface)

$$N_2\dagger + X \rightarrow N_2\dagger - - - X$$

with a sufficient lifetime to permit

(ii) attainment of the configuration required to cross to the potential surface corresponding to electronic excitation

$$N_2\dagger - - - X \rightarrow N_2^* - - - X \text{ (critical configuration)}$$

and (iii) separation of products on the excited potential surface with the collision partner receiving the electronic excitation energy

$$N_2^* - - - X \rightarrow N_2 + X^*.$$

The third step may be regarded as a resonance transfer of electronic excitation energy. Such transfers are known to occur readily when there is a close match of excitation energies. Since $N_2\dagger$ molecules in active nitrogen may have excitation energies considerably above the dissociation limits of most other molecules, perfect resonance should be possible between this excitation energy and the excitation energy of the continuous excited state of the collision partner. Thus, resonance transfer from $N_2\dagger$ to most other molecules should lead to dissociation of the collision partner.

If $N_2\dagger$ molecules can behave as discussed above, the rather puzzling results obtained from a study of the reaction of active nitrogen with mixtures of ammonia and ethylene (17) can be explained. At sufficiently high ammonia flow rates the limiting amount of ammonia decomposed did not change when ethylene was added, but the amount of HCN formed from ethylene was decreased in the presence of ammonia.[15] These results can be explained by the reaction scheme:

$$NH_3 + N_2\dagger \rightarrow N_2 + NH_3^* \rightarrow N_2 + NH_2 + H, \quad [1]$$

$$NH_2 + N \rightarrow N_2 + 2H, \quad [2]$$

$$N + C_2H_4 \rightarrow HCN + CH_3, \quad [3]$$

$$N + CH_3 \rightarrow HCN + 2H. \quad [4]$$

It is necessary to assume further that:

(i) the reaction of nitrogen atoms with radicals (reactions [2] and [4]) is very fast compared with the reaction with ethylene (reaction [3]);

(ii) reaction [1] is fast enough to give complete consumption of $N_2\dagger$ molecules when ammonia is present in sufficient excess, and the concentration of $N_2\dagger$ molecules is only about 15–20% of the concentration of atomic nitrogen;

(iii) the direct reaction between ammonia and nitrogen atoms is slow compared with reaction [3].

The first assumption receives support from theory and from experimental

[15]*Recent work by Armstrong and Winkler has shown that an increase in voltage across the nitrogen discharge, with other operating conditions constant, caused a marked increase in the ratio of the maximum amount of ammonia decomposed to the maximum yield of hydrogen cyanide from ethylene. This behavior gives strong support to the assumption of two reactive species in active nitrogen.*

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observations in other reactions (see below). The third is not unreasonable in view of the behavior of other simple hydrides, e.g. H_2, H_2O, CH_4, all of which are relatively inert to nitrogen atoms. The main reasons for the inertness appear to be (i) the endothermicity of hydrogen abstraction, (ii) the absence of long-lived complexes between these molecules and nitrogen atoms (15).

Of the reactants that have been studied so far, ammonia appears to be the only molecule that reacts fast with $N_2\dagger$ and slowly with N atoms. However, the observation of the first property is in large measure due to the second. Of the hydrocarbons studied, methane, ethane, and neopentane are the most inert to active nitrogen. Methane reacts to a significant extent only at such high temperatures that complications due to secondary hydrogen atom reactions obscure the results (15). The ethane and neopentane reactions appear to suffer a change in mechanism in going from low to high temperatures, as inferred from the observed activation energies (15). The simplest explanation seems to be that the low temperature, low activation energy reaction takes place by a mechanism similar to that suggested for ammonia, e.g.

$$N_2\dagger + C_2H_6 \rightarrow C_2H_5 + H + N_2,$$
$$N + C_2H_5 \rightarrow HCN + CH_3 + H,$$
$$N + CH_3 \rightarrow HCN + 2H,$$

and the high temperature, high activation energy reaction by the direct attack of nitrogen atoms.[16]

To explain the formation of secondary products in the fast reactions of other hydrocarbons with active nitrogen, it is necessary to assume (15) that reactions between nitrogen atoms and nitrogen atom – reactant complexes of the type

$$N + N.X \rightarrow N_2 + X^*$$

occur quite readily. The occurrence of these reactions makes it difficult to detect any contribution from the essentially similar reactions of the type

$$N_2\dagger + X \rightarrow N_2 + X^*.$$

In addition to resonance transfers, $N_2\dagger$ molecules might conceivably take part in two types of direct reactions: those that form two molecules of hydrogen cyanide and those that form one molecule of hydrogen cyanide and a nitrogen atom. However, reactions of the type

$$N_2\dagger + C_2H_2 \rightarrow 2HCN + (E + 8) \text{ kcal.},$$ [17]
$$N_2\dagger + C_2H_4 \rightarrow 2HCN + H_2 + (E - 50) \text{ kcal.},$$

where E is the excitation energy of $N_2\dagger$ above the lowest vibrational level, are probably very slow compared with the nitrogen atom reaction; propylene and the butenes preferentially lose only one carbon atom in the primary reaction to yield ethylene and propylene respectively as main products. Since the binding in the highest observed vibrational level of N_2 is tighter than that in

[16] *At sufficiently high temperatures, the ethane reaction becomes fast enough to go to virtual completion in the time spent in the reaction vessel. The limiting yields of HCN obtained agreed reasonably well with Wrede gauge measurements of the N atom concentration.*

[17] *See Ref. 15 for energy values used in calculating heats of reactions.*

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Cl_2, both as regards the dissociation energy and the force constant,[18] it might be expected that the activation energy for addition of $N_2\dagger$ to a double bond would be of the same order as that for the addition of molecular halogen, i.e. 20 to 30 kcal. (21).

Simple hydrocarbon radicals are formed as intermediates in many nitrogen atom reactions. Reactions of the type

$$N_2\dagger + CH_3 \rightarrow N + HCN + H_2 + (E-112) \text{ kcal.}$$

will probably be endothermic and should have a significant energy barrier. In addition they are spin disallowed[19] (see below) and should be slow compared with reactions of the type

$$N + CH_3 \rightarrow HCN + 2H + 10 \text{ kcal.}$$

These considerations make it appear unlikely that $N_2\dagger$ molecules would form much hydrogen cyanide by taking part in direct reaction.

THE ROLE OF SPIN CONSERVATION IN NITROGEN ATOM REACTIONS

The possible importance of electron spin conservation in reactions of atomic nitrogen has been suggested by Walsh (67). Nitrogen atoms in the ^4S state have three unpaired electron spins, and several features of the unified mechanisms suggested in a subsequent paper (15) make it appear likely that reactions that conserve spin occur more readily than those that do not.

The theoretical principle of spin conservation (69) says that the total spin of collision partners must remain unchanged before and after collision. The approximation on which it is based is only justified if the interaction between spin and orbital angular momentum is small. It is therefore similar to the prohibition of intercombinations between states of different multiplicities in the spectroscopic selection rules and applies only to light atoms that show Russell–Saunders coupling. The implications of spin conservation can be seen most clearly by the description in terms of potential surfaces given by Laidler and Shuler (41) in an excellent review of reactions involving excited electronic states.

When two molecules with spin vectors S_1 and S_2 approach each other their interaction may be represented by a set of potential surfaces with different spin labels given by the quantum number S where, by the usual vector sum rules, S can have the values

$$S = (S_1+S_2)(S_1+S_2-1)(S_1+S_2-2) \ldots (|\, S_1-S_2\,|)\,.$$

Since the molecules approach at random so far as the direction of their spin vectors is concerned, the relative probability that they interact on a potential surface of spin S will be given by the multiplicity $2S+1$. For a reaction that

[18] *Neglecting anharmonicity, the ratio of the force constants is* $k_{Cl_2}: k_{N_2\dagger} = 0.3$ *and the heats of dissociation are 2.5 ev. and 3.2 ev. for* Cl_2 *and* $N_2\dagger$ *respectively, where the values for* $N_2\dagger$ *have been taken for the highest observed vibrational level of the ground state (28).*

[19] *Spin allowed reactions of the type*

$$N_2\dagger + CH_3 \rightarrow N(^2D) + HCN + H_2 + (E-169) \text{ kcal.}$$

should have a high energy barrier.

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reaches completion on a given potential surface, it must be possible to obtain the corresponding value of S from the vector sum of the spin vectors of the products.

It seems likely (15) that a change of spin occurs in many of the reactions of active nitrogen. It is quite important therefore to consider the probability of crossing from one potential surface to another with a change of spin. Estimates of this probability have been made directly from the Landau–Zener equation using values for spin-orbital interaction energy, etc., determined from atomic spectra, and by calculating back from the observed transmission coefficients of reactions in which a change of spin occurs. Laidler and Shuler (41) have reviewed the rather scanty kinetic data and conclude that when a change of spin occurs in reactions involving light atoms the transmission coefficient is probably always less than 10^{-4}. However, direct estimates from spectroscopic data (62) indicate that it might be as high as 0.1. The discrepancy may be explained by partial cancellation of the larger contributions to the interaction energy caused by the rapid precession of orbital angular momenta, etc., (62). However, the accurate evaluation of transmission coefficients requires a high degree of precision in the determination of activation energies and complete faith in the statistical methods of the theory of absolute reaction rates, so that the extent to which such cancellation will occur is uncertain. A lower limit for the probability of a change in spin during collision in systems containing nitrogen may be estimated from the absence of Vegard–Kaplan bands in the spectrum of the afterglow. The radiation lifetime of the $A\,^3\Sigma$ state is between 10^{-3} and 10^{-4} sec. (47) and it is probably safe to assume that the collision rate between an A molecule and other molecules was less than 10^7/sec. in the spectroscopic studies. Hence, the probability of a change in spin during collision must have been at least 10^{-3} to 10^{-4}.

There are, as yet, no data for nitrogen atom reactions that are sufficiently accurate to permit calculation of transmission coefficients. Long-lived collision complexes are probably formed in several nitrogen atom reactions (15). These can only survive as long as there is a redistribution of the translational energy of the collision among the internal degrees of freedom of the complex. This redistribution should result in a greatly increased chance of crossing from one potential surface to another with a change of spin, since the complex may pass through the critical configuration many times during its lifetime. It is quite possible that, for these reactions, formation of the complexes is rate-determining, so that the kinetics will give no information about restrictions on a change of spin. Nevertheless, nitrogen atom reactions do provide quite good qualitative evidence that there is a restriction on a change in spin.

For example, the mechanism of the reaction of nitrogen atoms with ethylene is probably (15)

$$N + C_2H_4 \rightarrow HCN + CH_3, \qquad [3]$$

$$N + CH_3 \rightarrow HCN + 2H. \qquad [4]$$

Reaction [3] involves a change of spin; the reactants approach on a quartet surface (three unpaired spins) and the products separate on a doublet surface

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(one unpaired spin). Reaction [4] conserves spin if the interaction takes place on the triplet surface (vector sum of two unpaired spins). Since interaction can also occur on a quintuplet surface (four unpaired spins), reaction [4] will be spin-allowed for three out of every eight collisions. There is no indication that, although fast (61), the reaction

$$CH_3 + C_2H_4 \rightarrow C_3H_7$$

occurs to any extent in the nitrogen atom reaction with ethylene, even in the presence of excess ethylene. Hence, the reaction [4] must be much faster than reaction [3]. The difference in rate can be explained most easily by a restriction on the required change of spin in reaction [3].

Again, the reaction

$$N + CH_3 \rightarrow HCN + H_2 \qquad [5]$$

is much more favorable energetically than reaction [4], and might be expected to occur preferentially since there is good evidence that movement of hydrogen atoms occurs easily in nitrogen atom reactions (15). However, to explain the observed products of the ethylene and the propylene reactions with active nitrogen, it is necessary to assume that reaction [4] predominates. The most obvious reason for this appears to be that reaction [5] does not conserve spin.

The most plausible mechanism to account for the quite significant amounts of acetylene formed in the ethylene reaction appears to be (15)

$$N + N.C_2H_4 \rightarrow N_2 + C_2H_4^*, \qquad [6]$$

$$C_2H_4^* \rightarrow C_2H_2^* + H_2, \qquad [7]$$

$$C_2H_2^* \rightarrow C_2H_2, \qquad [8]$$

where $C_2H_4^*$ and $C_2H_2^*$ represent ethylene and acetylene in electronically excited triplet states and $N.C_2H_4$ is a collision complex. From quenching experiments with excited metal atoms, reaction [7] is known to occur when the excitation energy is sufficiently high and it has already been pointed out (41) that this is a good example of spin conservation.[20] Reaction [6] would have to compete with the energetically more favorable reaction

$$N + N.C_2H_4 \rightarrow N_2 + C_2H_4. \qquad [9]$$

Both reactions [6] and [9] are spin-allowed. However, reaction [6] should occur three times as often, other things being equal, since it will occur when the original interaction takes place on a triplet surface, while reaction [9] should take place on a singlet surface.

Rather similar mechanisms probably account for the formation of unsaturated hydrocarbons as secondary products of the reactions of both the alkyl halides and the saturated hydrocarbons with active nitrogen (15). The preferential formation of unsaturated hydrocarbons, particularly the formation of acetylene, is very difficult to understand unless spin conservation is important in these reactions.

[20]*Without calling on spin conservation, it is difficult to see how reaction* [7] *could compete with the spin disallowed deactivation reaction*

$$C_2H_4^* \rightarrow C_2H_4.$$

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APPENDIX. DEACTIVATION OF VIBRATIONALLY EXCITED NITROGEN MOLECULES

Let M_v be the concentration of excited molecules in the vth vibrational level at time t. Then, on the reasonable assumptions that thermal excitation can be neglected, and that collisions in which only one quantum of energy is transferred are much more likely than those in which several quanta are transferred, the rates of change of the various M_v values with time are given by

$$dM_v/dt = K_{v+1}\,M_{v+1} - k_v M_v, \qquad v = 1, 2, \ldots (n-1), \qquad [I]$$

where n is the highest level excited, and k_v is the rate constant for deactivation of the vth level,
and

$$dM_n/dt = -k_n M_n, \qquad [II]$$

$$dM_0/dt = k_1 M_1. \qquad [III]$$

If, for simplicity, it is assumed that $k_v = k$ for all values of v, and that initially

$$t = 0, \qquad M_n{}^0 = M_n, \qquad M_v = 0 \text{ if } v \neq n,$$

then it can be shown that the solution of equations [I], [II], and [III] is

$$M_{n-j}/M_n{}^0 = x^j e^{-x}/(j!), \qquad j = 0, 1, \ldots (n-1),$$

and

$$M_0/M_n{}^0 = 1 - \sum_{j=0}^{n-1} (M_{n-j}/M_n{}^0)$$

where x stands for kt.

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[21]*A series of papers by Strutt (Lord Rayleigh) in Proc. Roy. Soc., 1911–1922, discuss many interesting observations on active nitrogen.*

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CONDUCTANCES OF LITHIUM NITRATE SOLUTIONS IN ETHYL ALCOHOL AND ETHYL ALCOHOL - WATER MIXTURES AT 25.0°C.[1]

By A. N. Campbell and G. H. Debus[2]

ABSTRACT

The conductances of solutions of lithium nitrate in 30, 70, and 100 weight per cent ethyl alcohol have been determined at concentrations ranging from 0.01 molar up to saturation, at 25°C. The densities and viscosities of these solutions have also been determined. The data have been compared with the calculated conductances obtained from the Wishaw–Stokes equation. The agreement is fairly good up to, say, 2 *M*, for all solvents except absolute alcohol. In the latter solvent there is no value of å, the distance of closest approach, which will give consistent values of the equivalent conductance. In passing from pure water to pure alcohol, the value of å increases progressively and this we attribute to a change in the solvation of the lithium ion from water molecules to alcohol molecules. Some further calculations incline us to the view that the nitrate ion, as well as the lithium ion, is solvated to some extent, at least in alcohol.

The work of this laboratory for several years past has been directed to the determination of the electrical conductances of concentrated aqueous solutions of various electrolytes (4). More recently we have compared our experimental results with those calculated by means of the Wishaw–Stokes equation (10). The agreement between calculated and observed values, though far from exact, has nevertheless been sufficiently close to be very striking, so much so that we are convinced that the quantity å, the "distance of closest approach", is a real quantity, at least in so far as such theoretical concepts can ever be considered real. The constant occurrence of this quantity in expressions for the calculation of activity coefficients also lends support to this view, although the numerical values obtained by the two methods do not often agree with another.

The remaining quantity introduced into the Wishaw–Stokes equation, viz., the relative viscosity, is less satisfactory. Unquestionably, an ion moves less rapidly in a more viscous medium but the precise nature of the resistance to its motion is rather indefinite and certainly it is not measured quantitatively by the bulk viscosity. The approximate agreement between observed and calculated results, however, shows that, in most cases, the bulk viscosity is an approximation to the truth.

The vexed question of viscosity can be avoided by confining investigation to solutions whose viscosity does not differ greatly from that of the solvent; such solutions are not necessarily dilute. When, under such conditions, the observed (equivalent) conductance is found to be less than the calculated, Robinson and Stokes (8) attribute this to ion-pair formation, and they have had some success in the calculation of an ionization constant.

[1]*Manuscript received May 14, 1956.*
Contribution from the Chemistry Department of the University of Manitoba, Winnipeg, Manitoba.
[2]*National Research Council of Canada Postdoctorate Fellow.*

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In our work on the conductance of aqueous lithium nitrate solutions, the agreement between calculated and observed conductance remains good up to the very high concentration of 6 *M*. This we attributed to the absence of ion-pairs and this again could be very well accounted for as due to the complete insulation of the lithium ion by its firmly bound water of hydration. We presumed, however, that if we added alcohol, in increasing amounts, this would have the dual effect of stripping water from the hydration sheath and of lowering the dielectric constant and both these effects would tend to favor ion-pair formation. We expected, therefore, that at a rather sharply defined alcohol concentration deviation would commence between the calculated curve of conductance and the observed one, in the direction of the observed becoming less than the calculated. It was on this basis that the present work was undertaken. It should be said at once that none of these expectations has been realized and that the behavior of lithium nitrate solutions in alcohol and alcohol–water mixtures requires a totally different explanation.

EXPERIMENTAL

Our technique for conductance and viscosity determinations has been described elsewhere (4). Solvents consisting of 30 and 70 weight per cent alcohol were obtained by diluting a commercial 95% ethyl alcohol, which had been purified by distillation from freshly ignited lime. A sufficient volume of each solvent to complete the series of measurements was made up and stoppered off. For absolute alcohol as a solvent, a so-called "absolute" alcohol, obtained from Canadian Industrial Alcohols and Chemical Limited ("Guaranteed to meet the Specifications of the British and U.S. Pharmacopoeia"), was treated with magnesium ethoxide and distilled through a Podbelniak column. The alcohol content of the solvents was checked by density and dielectric constant determinations. The latter, extrapolated to zero frequency, were found to be in good agreement with those of Åkerlöf (1). Measurements of conductance, density, and viscosity of solutions in absolute alcohol were all made in stoppered vessels since absolute alcohol is notoriously hygroscopic. This precaution was not necessary with the diluted alcohols.

EXPERIMENTAL RESULTS

The B, B_1, and B_2 values of the Wishaw–Stokes equation are calculated for each solvent, from the viscosity, dielectric constant, and temperature, and are given at the head of each table. Our results, both observed and calculated, are contained in Tables I, II, and III. In Figs. 1, 2, and 3, the equivalent conductances, observed and calculated for the most favorable value of å (see Table IV), are plotted against molar concentration. Fig. 4 represents similar results obtained by Klochko and Grigorjew (7) for lithium nitrate in methyl alcohol, and calculated by us in the same way.

DISCUSSION OF RESULTS

The viscosity of ethyl alcohol – water mixtures is anomalous. The results of Bingham and Jackson (3) show a maximum viscosity at about 50% alcohol, where the mixture is 2.685 times as viscous as water and 2.189 times as viscous

TABLE I

$LiNO_3$ IN 30% C_2H_5OH+70% H_2O, T = 25.00°C.
B_1 = 0.3333, B_2 = 28.04, B = 0.3726

Wt. % $LiNO_3$	C, mol./l.	$d_4^{25°}$	η/η_0	$\kappa\times10^6$	Λ_{exp}	$\Lambda\eta/\eta_0$	Λ_{calc}			
							å = 4	å = 4.5	å = 5	å = 6
0	0	0.9507	1.000	—	—	—	51.5†	51.5†	49.50	48.0
0.1370	0.01891	0.9516	1.001	819.3*	43.34	43.38	—	46.47	—	43.35
0.3080	0.04256	0.9526	1.002	1801.0*	42.32	42.40	—	44.57	—	41.74
0.6230	0.08623	0.9543	1.004	3471.8*	40.26	40.42	—	42.58	—	40.06
3.711	0.5231	0.9720	1.033	18711	35.77	36.59	35.30	36.01	34.47	34.37
7.359	1.059	0.9920	1.073	32726	31.91	32.83	30.62	31.85	—	30.75
11.967	1.769	1.019	1.128	47925	27.10	30.27	27.24	28.53	27.91	28.14
15.013	2.259	1.038	1.187	55911	24.74	29.09	24.97	26.26	—	25.94
19.327	2.985	1.065	1.288	64403	21.57	27.50	22.06	23.27	22.80	23.03
24.727	3.951	1.102	1.472	70553	17.86	26.04	18.40	19.42	—	19.21
27.958	4.561	1.125	1.613	71798	15.74	25.14	16.33	17.14	16.93	17.03
28.565	4.680	1.130	1.665	71780	15.33	25.03	—	16.62	—	16.42
33.37	5.643	1.166	1.968	70558	12.51	24.38	—	13.54	13.23	13.25
38.04	6.639	1.203	2.445	67439	10.16	24.60	—	10.46	—	10.18
43.33	7.850	1.249	3.226	61885	7.88	25.17	—	7.55	—	7.24‡
48.79	9.188	1.298	4.450	55222	6.01	26.74	—	5.14	—	4.88‡
53.66	10.48	1.347	6.48	48498	4.63	30.00	—	3.38	—	3.13‡
54.15	10.62	1.352	6.77	47837	4.51	30.53	—	3.22	—	2.98‡

*Corrected for solvent.
†Whitman and Hurt's value of Λ_o.
‡κå$_{max}$ = 6.

TABLE II

$LiNO_3$ IN 70% C_2H_5OH+30% H_2O, T = 25.00°C.
B_1 = 0.6798, B_2 = 38.05, B = 0.4724

Wt. % $LiNO_3$	C, mol./l.	$d_4^{25°}$	η/η_0	$\kappa\times10^6$	Λ_{exp}	$\Lambda\eta/\eta_0$	Λ_{calc}		
							å = 6.5	å = 7.5	å = 8.5
0	0	0.8634	1.000	—	—	—	37.20	36.7	36.4
0.0903	0.01132	0.8640	1.004	364.9*	32.23	32.59	32.07	31.76	31.75
0.1981	0.02484	0.8644	1.009	753.6*	30.30	30.57	30.32	30.12	29.98
0.6823	0.08582	0.8672	1.029	2290.4	26.69	27.46	26.76	26.89	26.85
1.009	0.1271	0.8691	1.043	3244.6	25.54	26.64	25.44	25.62	25.63
1.908	0.2419	0.8740	1.073	5629	23.28	24.98	23.05	23.41	23.49
4.274	0.5502	0.8877	1.160	10763	19.56	22.69	19.24	19.69	19.82
6.378	0.8324	0.8999	1.250	14409	17.31	21.64	16.76	17.31	17.42
9.484	1.263	0.9182	1.386	18557	14.69	20.36	13.98	14.39	14.67
12.78	1.740	0.9384	1.579	21487	12.35	19.50	11.38	11.68	11.72
16.99	2.379	0.9654	1.875	23588	9.91	18.58	8.68	8.80	8.79
19.54	2.785	0.9822	2.108	24080	8.65	18.23	7.24	7.29	7.23†
23.92	3.510	1.012	2.610	23917	6.81	17.74	5.17	5.18†	5.12†
28.51	4.324	1.045	3.359	22751	5.26	17.67	3.46†	3.39†	3.35†
32.31	5.034	1.074	4.194	21503	4.19	17.57	2.41†	2.37†	2.36†
37.22	6.012	1.113	5.723	19605	3.26	18.66	1.46†	1.43†	1.42†

*Corrected for solvent.
†κå$_{max}$ = 6.

as alcohol. This behavior indicates an interaction between the components of the mixture which is unfortunate for the purpose of this investigation.

In order to use the Wishaw–Stokes equation, it is necessary to know the value of Λ_0, and this is usually not known for temperatures other than 25° and for solvents other than water. For pure alcohol, we fortunately possess some very

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TABLE III

$LiNO_3$ IN C_2H_5OH AT 25.00°C.
$B_1 = 1.330$, $B_2 = 89.91$, $B = 0.5908$

Wt. % $LiNO_3$	C, mol./l.	$d_4^{25°}$	η/η_0	$\kappa \times 10^6$	Λ_{exp}	$\Lambda\eta/\eta_0$	Λ_{calc}				
							å = 2	å = 4	å = 6	å = 8	å = 10
0	0	0.7850	1.000	—	42.7*	42.7	42.7	42.7	42.7	42.7	42.7
—	0.000219	—	—	—	40.25*	—	40.63	—	—	40.74	40.75
—	0.001285	—	—	—	36.52*	—	37.78	—	—	38.27	38.62
—	0.002407	—	—	—	34.39*	—	36.11	36.85	36.72	26.97	37.21
2.158	0.2503	0.7997	1.276	3073.5	12.28	15.67	6.10	—	—	16.22	17.46
4.500	0.5321	0.8154	1.591	4824.7	9.07	14.43	—	7.43	9.11	9.16	—
7.457	0.9916	0.8399	2.209	6437.1	6.49	14.34	—	3.18	5.09	6.09	—
12.43	1.567	0.8689	3.215	7325.3	4.68	15.05	Negat.	—	—	2.89†	—
16.33	2.121	0.8958	4.365	7534.6	3.55	15.50	Negat.	0.73	1.29†	1.22†	—
19.49	2.593	0.9174	5.617	7387.3	2.85	16.01	Negat.	0.40†	0.64†	0.64†	—
23.39	3.206	0.9450	7.51	7114.5	2.22	16.67	Negat.	0.15†	0.19†	0.19†	—

*Copley, Murray-Rust, and Hartley (6).
†$\kappa å_{max} = 6$.

TABLE IV

MOST FAVORABLE VALUES OF å

Solvent	å in Angstroms
Water	4.5
30% alcohol	6.0
70% alcohol	7.5 to 8.5
100% alcohol	No value gives consistent results

accurate conductance figures for dilute solutions of lithium nitrate, due to Copley, Murray-Rust and Hartley (6), and by treating these figures in the usual way we arrived at 42.7 mhos as the value of Λ_0 in alcohol at 25° C. For 30% alcohol, figures are available by Whitman and Hurt (9), which yield 51.5 mhos as the value of Λ_0. Our own figures for the relatively high concentrations of 0.01891, 0.04256, and 0.08623 N gave $\Lambda_0 = 48.5 \pm 1.0$ mhos, and this value fits the Wishaw–Stokes equation better than the higher figure; we have used 49.5 and 48.0 in calculation. For 70% alcohol we used our own data for solutions of 0.01132, 0.02484, and 0.08582 N, and from these we estimate Λ_0 as 36.7 ± 1 mhos; we have calculated with 37.20, 36.7, and 36.4. However, none of these Λ_0 values has any great accuracy and they must be considered as semiempirical parameters. It is not surprising that Λ_0 in 70% alcohol should be less than Λ_0 for pure alcohol, since this solvent is more viscous than pure alcohol, but the fact that the 70% solvent shows a lower Λ_0 than 30% alcohol cannot be explained purely on the grounds of viscosity, since the 30% alcohol is slightly more viscous than the 70% mixture. It seems obvious to us, from this and other observations, that the solvation sheath of the lithium ion changes from a predominantly water sheath to a predominantly alcohol sheath, between 30 and 70% alcohol.

A recent treatment by Amis (2), however, would seem to indicate that this deduction is not inevitable, in other words, that the occurrence of a minimum

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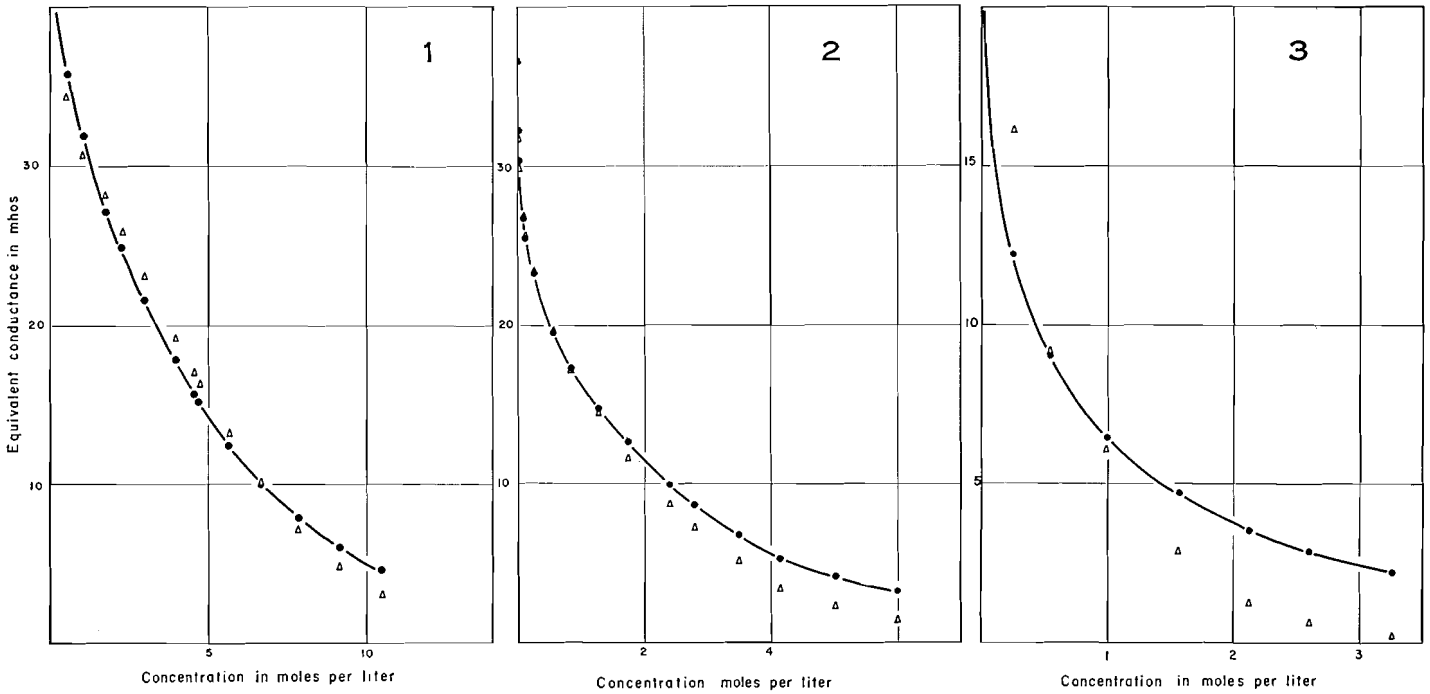

FIG. 1. $LiNO_3$ at 25.00°C. Solvent: 70 wt-% H_2O, 30 wt-% C_2H_5OH. ● Experimental values. △ Calculated values; å = 6, Λ_0 = 48.
FIG. 2. $LiNO_3$ at 25.00°C. Solvent: 30 wt-% H_2O, 70 wt-% C_2H_5OH. ● Experimental values. △ Calculated values; å = 7.5, Λ_0 = 36.7.
FIG. 3. $LiNO_3$ at 25.00°C. Solvent: C_2H_5OH. ● Experimental values. △ Calculated values; å = 8, Λ_0 = 42.7.

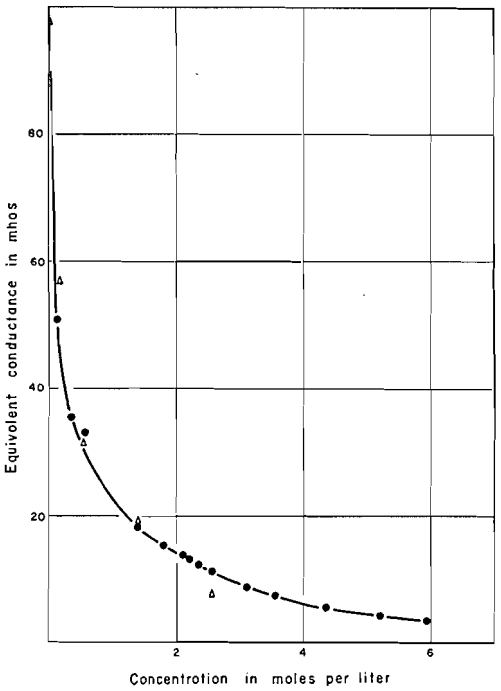

FIG. 4. $LiNO_3$ at 25.00°C. Solvent: CH_3OH. ● Experimental values. △ Calculated values; å = 8, Λ_o = 98. Results of M. A. Klochko and I. G. Grigorjew.

value of Λ_0, when Λ_0 is plotted against alcoholic content, may be merely a consequence of changes in viscosity, dipole moment, and dielectric constant. Amis gives the formula:

$$[1] \qquad \frac{\Lambda_0 \eta \mu}{D} = \text{constant}$$

where μ and D mean the dipole moment and dielectric constant, respectively. It is assumed that the dipole moment of a mixed solvent can be calculated by the mixture rule from the dipole moments of the constituents, thus:

$$[2] \qquad \mu = N_1\mu_1 + N_2\mu_2.$$

Since the dipole moments of water and of alcohol differ only slightly, the calculation is a very reasonable one, in this case. Using the unexceptionable data for Λ_0 in pure water, we obtain for the constant the value 0.023046, and using this constant we obtain Table V.

The figures for Λ_0 are far from agreeing but the calculated values show the same minimum as do the observed.

When considering the increase in å in passing from water to alcohol (see Tables I, II, and III), it seems natural to attribute this entirely to a change in lithium ion solvation but some afterthoughts incline us to think that the NO_3^- ion may not be as bare and unchanging as is sometimes supposed. The fol-

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TABLE V

Λ_0, OBSERVED AND CALCULATED, FOR MIXTURES OF ETHYL ALCOHOL AND WATER, AT 25°C.

Wt. % ethyl alcohol	D	η	μ	$\Lambda_{0_{calc}}$	$\Lambda_{0_{obs}}$
0.00	78.5	0.00893	1.84	—	110.1
30.00	61.1	0.0218	1.83	37.77	48.0
70.00	38.0	0.02037	1.77	24.29	36.7
100.00	24.3	0.0109	1.70	30.22	42.7

lowing formula, given by Robinson and Stokes (8), is derived on the assumption that the Stokes' viscosity law applies to the motion of an ion:

[3] $$r = (0.820 \mid Z \mid/\lambda^\circ\eta_0)(r/r_s) .$$

In this formula, r is the radius of the ion in solution, r_s is the so-called "Stokes radius", i.e. the radius if Stokes' law were rigorously obeyed, and λ° the limiting ionic conductance. Thus, (r/r_s) is an empirical correction factor depending on the value of r_s, designed to bring the Stokes' radius into line with that calculated by other methods. If it is assumed that the radius of the nitrate remains constant (no solvation) and that the correction factor remains the same in solvents other than water, we have the relation

[4] $$\lambda^\circ \propto 1/\eta_0.$$

Equation [4] is none other than Walden's rule, which is actually valid in many cases. Hence, knowing λ° in pure water at 25° C. (71.46 mhos for NO_3^- ion) it is possible to calculate λ° for NO_3^- ion in other solvents and hence by subtraction from Λ_0 to obtain λ° for Li^+ ion. The results are contained in Table VI.

TABLE VI

IONIC CONDUCTANCES IN VARIOUS CONCENTRATIONS OF ALCOHOL

Wt. % alcohol	$\lambda^\circ_{NO_3^-}$	$\Lambda_{0_{exp}}$	$\lambda^\circ_{Li^+}$
0.00	71.46	110.1	28.68
30.00	29.27	48.0	18.73
70.00	31.32	36.7	5.38
100.0	58.54	42.7	−15.84

The negative value for $\lambda^\circ_{Li^+}$ in alcohol is impossible and this implies either that Equation [3] is incorrect in its application to water–alcohol mixtures or that the assumption of a constant radius for the nitrate ion is untenable, or that the correction factor is not constant.

Using the values of $\lambda^\circ_{Li^+}$ listed in Table VI, r_{Li^+} is now calculated from Equation [3], while $r_{NO_3^-}$ is calculated from the water data. There is some uncertainty about the latter value, since the correction factor (r/r_s) is large. The calculation is impossible for pure alcohol since $\lambda^\circ_{Li^+}$ has a negative value (Table VI). The results are collected in Table VII.

For the three solvents of Table VII, it might be assumed that the difference

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TABLE VII

EFFECTIVE RADII IN SOLUTION OF Li^+ AND NO_3^- IONS

Wt. % alcohol	Radii in solution, Å		$r_{NO_3^-}+r_{Li^+}$, Å	å from Stokes' equation, Å
	Li^+	NO_3^-		
0.00	3.7	3.0	6.7	4.5
30.0	3.4	3.0	6.4	6.0
70.0	7.5	3.0	10.5	7.5

between å and $r_{Li^+}+r_{NO_3^-}$ represented "penetration" but, since absolute alcohol yields an impossible result, we consider it more likely that the fallacy lies in assuming the NO_3^- ion has a constant radius irrespective of the solvent. If it is admitted that the nitrate ion is solvated like the lithium ion, though not to the same extent, we have an obvious explanation of the failure of theory to agree with experiment.

In the two aqueous alcohols the agreement with the Wishaw–Stokes equation is good up to 2 *M*, using for å the value 6.0 in 30% alcohol, and 7.5 in 70% alcohol. No assigned value of å, however, gives good results in pure alcohol. We have used the value å = 8.0, but reference to Table III will show that all values of å are equally unsatisfactory. For solutions in pure water we previously used å = 4.5 and obtained excellent agreement (5). We have alluded in the introduction to the somewhat doubtful nature of the viscosity correction

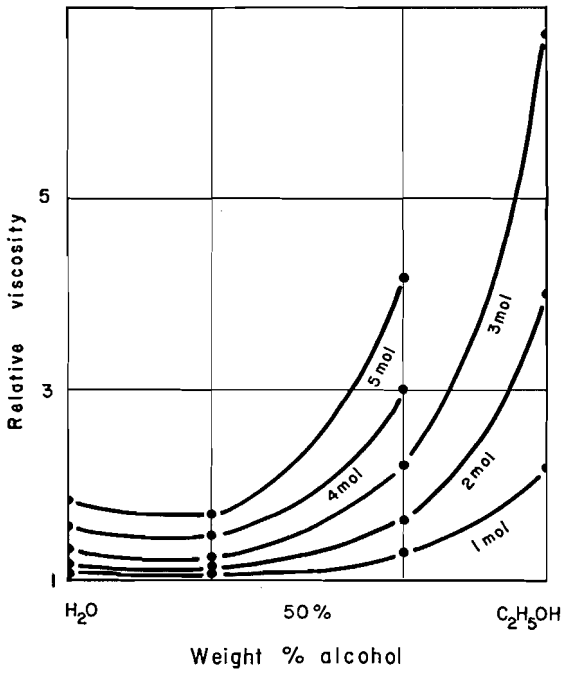

FIG. 5. Relative viscosity vs. weight per cent alcohol in the solvent.

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and we see in this a possible explanation of the anomalous behavior of solutions in anhydrous alcohol. Fig. 5 is intended to illustrate this point. In this figure, the relative viscosity, that is to say the viscosity of the solution divided by the viscosity of the solvent, is plotted for interpolated concentrations of 1, 2, 3, 4, and 5 molar, against weight per cent alcohol in the solvent. It will be observed that the relative viscosity increases enormously at the higher alcohol concentrations; thus, a 3 M solution in absolute alcohol is seven times as viscous as the solvent, while in 70% alcohol it is only about twice as viscous. It may be that at these very high relative viscosities, the simple expedient of dividing the calculated equivalent conductance by the relative viscosity is no longer a permissible approximation.

In Fig. 6 the (observed) specific conductance is plotted against molar

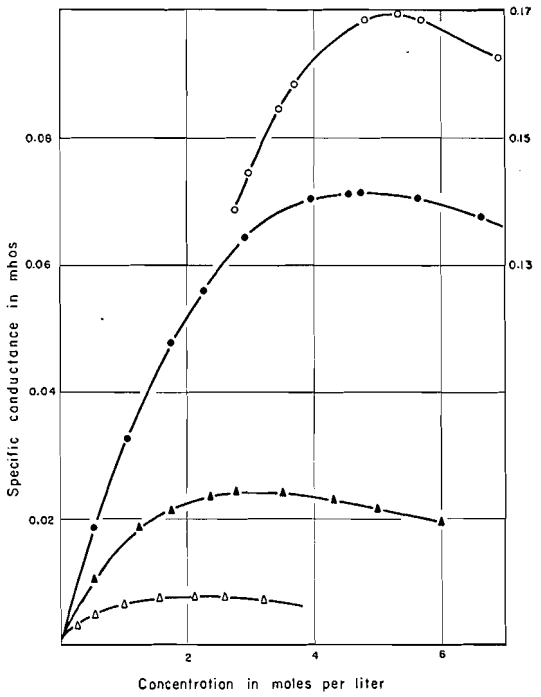

FIG. 6. $LiNO_3$. ○ H_2O. ● 70% H_2O+30% C_2H_5OH. ▲ 30%] H_2O+70% C_2H_5OH. △ C_2H_5 OH.

concentration for pure water and the three alcoholic solutions. In all four cases, the specific conductance passes through a maximum. The concentration at which the maximum occurs decreases as we pass from pure water to pure alcohol; the curve also becomes much flatter. The maximum occurs at (approximately) 5 M for pure water, at 2 M for pure alcohol, and at intermediate molarities for intermediate strengths of alcohol.

As usual in our work, we have plotted in Fig. 7 Λ_0 against $\log c$, and obtained

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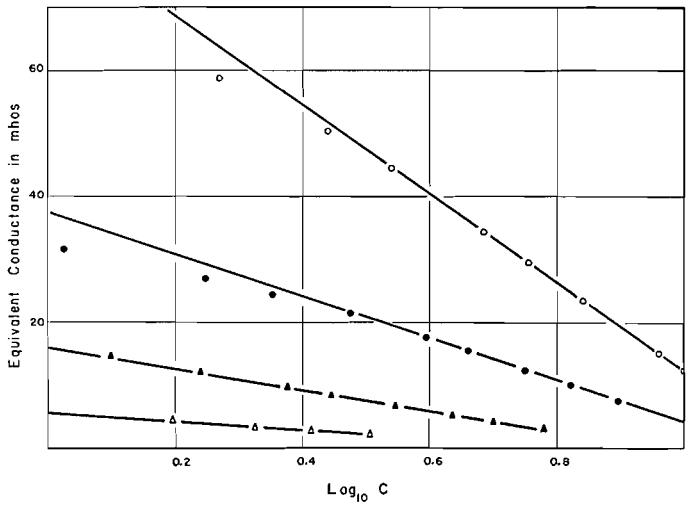

FIG. 7. ○ H_2O. ● 70% H_2O+30% C_2H_5OH. ▲ 30% H_2O+70% C_2H_5OH. △ C_2H_5OH.

the usual straight line. There is no theoretical justification for doing this and it may be contended that any function plotted logarithmically will give a straight line; admittedly, the variation is reduced by this procedure. We still think, however, that this explanation is a little too facile for a relationship which we have hardly ever found to fail.

The main conclusion of this work is that, despite the lowered dielectric constant in alcohol and alcohol–water mixture, lithium nitrate solutions do not form ion-pairs in these solvents. If the å values used by us in the calculations of Λ are accepted as having real physical significance, our deduction receives immediate support; with these very large distances of closest approach, the ions can never get close enough for ion-pair formation, despite the fact that this minimum distance is increased by the reduced dielectric constant. The increase in the distance of closest approach is explained as due to a change of the solvation sheath from water to alcohol molecules. We attempted a direct experimental confirmation of this by determining the (short wave) infrared absorption of solutions of lithium nitrate in water and in alcohol but, over the range of wave-length available to us, we could detect no difference in the vibration frequencies of the OH-group or its first two harmonics. This, of course, is no argument against the occurrence of solvated complexes since, if attachment is at the hydroxylic oxygen, as it presumably is, this would scarcely alter the frequency, since the hydrogen atom is so much lighter than the oxygen atom in any case.

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A DILATOMETRIC STUDY OF SOLID METHANOL-*d*[1]

By D. W. Davidson

ABSTRACT

With isopentane as the dilatometric liquid, CH_3OD was examined between 120°K. and the melting point. There is evidence of two transitions within the solid: one, in the vicinity of 158°K., appears to be a gradual transition, the other, at 163°K., a first-order one. The corresponding molar volume changes are 0.04 and 0.43 ml. A further change of volume of 2.67 ml./mole occurs at the melting point. These results are compared with recent dilatometric results for CH_3OH and discussed with reference to the available calorimetric data. The molar volume of CH_3OD is slightly greater than that of CH_3OH in both liquid and solid forms.

The presence of a phase transition within solid methanol has been known for some time (4, 5). Recently the nature of the transition has been investigated in a number of studies on solid methanol in which a variety of experimental approaches has been used. These have included a new calorimetric study by Staveley and Gupta (6), an X-ray examination of the low and high temperature modifications of the solid by Tauer and Lipscomb (8), and an investigation by Cooke and Drain (1) of the proton magnetic resonance line width. In a recent dilatometric study of CH_3OH, Staveley and Hogg (7) found evidence of *two* transitions only a few degrees apart. As long as the presence of only one transition had been assumed, it had usually been classified as a λ-type transition, rather than a first-order one, largely as a result of heat capacity measurements. Thus, when the sample was heated through the transition, thermal equilibrium was rapidly reached in the early stages of the transition but only slowly in the later stages (6). Now it appeared that the thermal measurements had included contributions from two distinct transitions: one apparently a gradual, non-isothermal transition occurring in the vicinity of 156°K., the second, at 159°K., probably a typical first-order transition at which the change from the monoclinic to orthorhombic structure (8) took place.

The calorimetric study by Stavely and Gupta (6) appears to be the only published work on CH_3OD. The thermal behavior of CH_3OD in the vicinity of the heat capacity maximum showed the same anomalies as it did for CH_3OH. This suggests that there are two transitions in CH_3OD as well.

The present work was undertaken to check this possibility and, if possible, to throw some light on the nature of the lower temperature, gradual transition.

EXPERIMENTAL

The thermostat consisted of a heater-wound aluminum block, insulated and placed in a copper can which was mounted in a 5-gal. Dewar flask. Liquid nitrogen was admitted to the latter to a height kept roughly constant by a bimetallic thermoregulator with its tip just immersed in the nitrogen. This

[1]*Manuscript received June 5, 1956.*
Contribution from the Division of Applied Chemistry, National Research Council, Ottawa, Canada. Issued as N.R.C. No. 4037.

regulator controlled the compressed air supply which intermittently supplied liquid nitrogen from an external tank. A second regulator, mounted in the block, controlled the heater circuit. Temperature was measured by two copper–constantan thermocouples, one in the central air cavity of the block and one in the block itself. These thermocouples were calibrated by the Applied Physics Division of N.R.C. to an absolute accuracy of $\pm 0.2°$. A period of at least two hours was allowed for temperature equilibration after the thermostat had been set for a new temperature. In the region of the transitions a period of about five hours was allowed.

Because of the tendency of methanol to shatter the containing bulb when the solid is warmed, a carrot-shaped dilatometer bulb was used as an alternative to the method of Staveley and Hogg (7), who placed the sample in a separate loose tube within the dilatometer bulb. No shattering was encountered. A 1 meter length of calibrated 1 mm. capillary tubing was sealed to the large end of the bulb.

The dilatometric fluid was isopentane (Phillips Petroleum Co., 99 mole% minimum) which was distilled over calcium hydride; a middle fraction was used. The known densities of isopentane (2) were extended to the lowest temperature required by following the change of volume of isopentane itself in the dilatometer.

The CH_3OD used contained less than 0.07% by volume of water, as determined by the Fischer reagent. Its infrared spectrum showed less than 1% CH_3OH. A quartz pycnometer of the type described by Kirshenbaum (3) in connection with studies of the density of D_2O, but of smaller (11 ml.) capacity, was constructed for the density determination. The value obtained ($d_4^{20} = 0.81252$) is a little lower than the value reported by Staveley and Gupta (6) (0.81269). Within the accuracy of the refractometer (~ 0.0002), the refractive index (n_D^{20}) was found to be identical with that of CH_3OH.

Like CH_3OH, CH_3OD readily supercools below the main transition temperature. To ensure the complete absence of the orthorhombic form at temperatures below this transition point, a thermal conditioning procedure similar to that used by Staveley and Hogg (7) was followed. All measurements were made with increasing temperature except for occasional tests of reversibility, particularly in the transition regions.

RESULTS

In Fig. 1 the molar volume of CH_3OD is plotted against temperature. The change in volume on melting is only slightly less for CH_3OD than for CH_3OH (see Table I). Both of these volume changes at melting were measured in the presence of isopentane, which is soluble in liquid methanol to the extent of about 1 mole % (7). This accounts for the lowering of the melting point, which is about a degree lower than the value 173.5_2°K. reported by Staveley and Gupta (6). A cooling curve run on CH_3OD itself gave a freezing point of 173.6°K.

The principal transition within the solid occurs at 163°K., some four degrees higher than in light methanol. The volume change is 0.43 ml./mole, again

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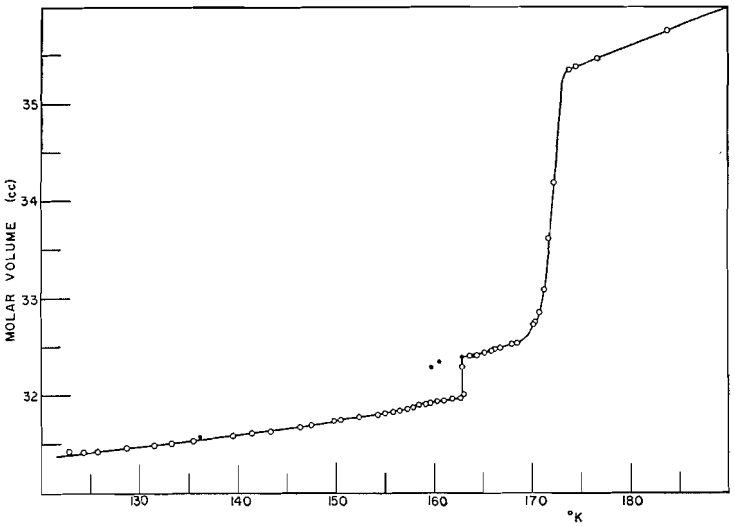

FIG. 1. Molar volume of CH_3OD.

TABLE I

	CH_3OH			CH_3OD		
	$\alpha-\alpha^1$	$\alpha^1-\beta$	Melting	$\alpha-\alpha^1$	$\alpha^1-\beta$	Melting
(*a*) Transition temperatures (°K.)						
Dilatometric method	156	159	—	158	163	(173.6)
Calorimetric method	157.8		175.4	161.1		173.5
(*b*) Molar volume changes (ml.)						
Dilatometric method	~0.14	0.49	2.75	~0.04	0.43	2.67
(*c*) Molar entropy changes (e.u.)						
Calorimetric method	1.08		4.31	0.97		4.18
(*d*) Ratio (*b*): (*c*) (ml./e.u.)		0.45*	0.638		0.44*	0.639

*See text.

lower than in CH_3OH (0.49). As indicated by the solid circles in Fig. 1, which are volumes obtained with cooling, the high temperature form readily supercools through this transition temperature.

A further change in volume (shown more clearly in Fig. 2) occurs in the vicinity of 158°K., two degrees higher than the gradual transition in CH_3OH. This transition in CH_3OD also appears to be a gradual one. The volume change appears with both increasing and decreasing temperature (the open and filled circles refer to increasing, the crosses to decreasing, temperature) with no sign of supercooling or hysteresis. The volume change (~0.04 ml./mole) accompanying this transition in CH_3OD is very small, even in comparison with the volume change near 156° in CH_3OH (~0.14 ml./mole).

In Table I the present dilatometric results are summarized and compared

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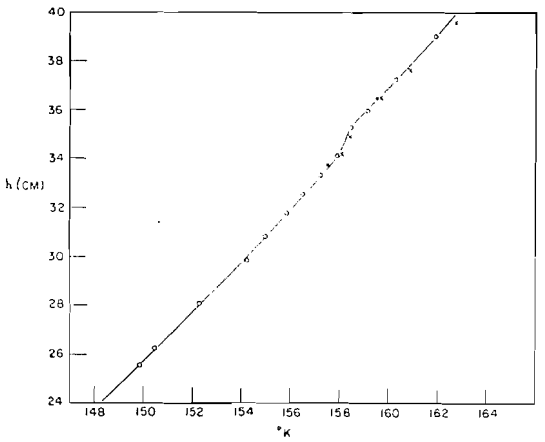

FIG. 2. Height of isopentane column vs. temperature in the region of the low temperature transition.

with the dilatometric data of Staveley and Hogg (7) and the calorimetric results of Staveley and Gupta (6). The low and high temperature transitions are called $\alpha-\alpha^1$ and $\alpha^1-\beta$ transitions respectively.

DISCUSSION

As far as the author is aware, no X-ray study of CH_3OD has yet been made. The similarity of CH_3OD to CH_3OH in its calorimetric and volumetric properties makes it likely that the transition at 163°K. corresponds to a change in crystal form from the monoclinic to the orthorhombic modification; the dimensions of the unit cells in the two modifications are probably not much different from the values given by Tauer and Lipscomb (8) for CH_3OH.

The smallness of the change in volume at the low temperature transition makes it difficult to establish whether or not the transition ends abruptly on the high temperature side. It does, however, appear to set in gradually at least two degrees below the temperature at which the coefficient of expansion reaches its maximum value (158°K.).

The ratios of the molar volume to the molar entropy changes at the melting point and at the first-order $\alpha^1-\beta$ transition are included in Table I. For the melting process this quantity is, within experimental error, the same for both methanol molecules. Since this ratio is a measure of the effect of pressure on the temperature of a first-order transition, this result provides additional evidence for the similarity in the crystal structure of the high temperature forms, and, incidentally, provides a consistency test for the four sets of experimental data.

In the case of the transitions within the solid, it is uncertain what fraction of the total entropy change should be assigned to each of the two transitions. It is apparent, however, that most of this entropy change should be assigned to the first-order $\alpha^1-\beta$ transition. If the whole of the entropy change is so assigned, the result is again that the volume to entropy ratios for the two

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molecules are the same. This result is also obtained if the same fraction of the total entropy change is assigned to the $\alpha-\alpha^1$ transitions in both molecules, but the large difference between the volume changes of the two molecules at this transition would seem to make this procedure of doubtful validity. It is difficult to avoid the conclusion that the entropy change at the $\alpha-\alpha^1$ transition is extremely small, perhaps no more than a few one-hundredths of an entropy unit.

The molar volume of CH_3OD is consistently larger than that of CH_3OH (Table II). In the liquid the ratio of molar volumes (1.0046 at 20°) is the same

TABLE II

MOLAR VOLUMES (ML.)

	Liquid (20°C.)	β-Solid (−110°C.)	α-Solid (−160°C.)
CH_3OH, dilatometric	40.488	32.25	30.96
CH_3OD, dilatometric	40.675	32.40	31.27
CH_3OH, X-ray		32.96±0.33	31.41±0.53
Ratio CH_3OD: CH_3OH	1.0046	1.005	1.010
Ratio D_2O: H_2O	1.0036 (25°C.)	1.0016 (0°C.)	

order of magnitude as this ratio for heavy and light water (1.0036 at 25°C.) (3) and the explanation is probably the same, i.e., slightly more regular hydrogen bonding exists in the deuterium-substituted liquid. Values of the molar volumes are also given for the two temperatures in the solid state at which Tauer and Lipscomb did their X-ray work. The dilatometric volumes are smaller than those calculated from the unit cell dimensions but the difference may not be sufficiently great to lie outside the limits of accuracy of the X-ray results.

The greater molar volume of CH_3OD in the solid is particularly evident in the α phase where the difference between the two methanol molecules amounts to 1%. The relatively large molar volume of methanol-*d* in this phase may account for the relatively small volume change at the $\alpha-\alpha^1$ transition. It may be that the lattice is sufficiently expanded in the α-modification that, as the transition region is approached, the further expansion that takes place to accommodate the transition need only be small.

Staveley and Hogg (7) have advanced the suggestion that the gradual transition in CH_3OH may be connected with the disappearance of an alternation in the positions of the methyl groups in planes parallel to the (010) face of the monoclinic crystal. This alternation had been proposed by Tauer and Lipscomb to explain the presence of faint "superlattice" lines in the X-ray pattern at −160°C. The results of the present work on CH_3OD are not inconsistent with this explanation. The small effect of deuterium substitution in the hydroxyl group on the transition temperature suggests that the hydroxyl group may not play an important part in the transition process.

The existence of the second transition in methanol and methanol-*d* is confirmed by recent dielectric work (9). There is a small, but well-defined, rise in

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the dielectric constant, as measured at radio frequencies, in the temperature region where the volume change occurs. This effect is particularly pronounced in CH_3OD.

ACKNOWLEDGMENTS

The author is indebted to Dr. L. C. Leitch for supplying the methanol-*d* and to Dr. I. E. Puddington for helpful discussions.

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DEUTERIUM MIGRATION DURING THE IONIZATION OF 1-BUTENE-4-d_3 BY ELECTRON IMPACT[1,2]

By W. A. Bryce and Paul Kebarle

ABSTRACT

The mass spectrum of CD_3—CH_2—CH=CH_2 has been measured in a 90° Nier-type mass spectrometer using 50-volt electrons. High resolution nuclear magnetic resonance measurements showed that the methyl group was fully deuterated and that there were no D-atoms located elsewhere in the molecule. This result was supported by infrared analysis. A comparison of the mass spectrum with that of CH_3—CH_2—CH=CH_2 shows that the total intensities of each group of C_4, C_3, C_2, and C_1 fragments are the same for both compounds. This indicates equal probabilities of C—C bond rupture in the dissociation of the corresponding parent ions. The distribution of fragments within the groups in the deuterated compound shows, however, that extensive migration of the D-atoms has occurred during ionization. Migration is also evident at much lower electron energies (approximately 15 ev.). The thermal cracking patterns of the two compounds, as determined by gas chromatographic analyses, are very similar.

INTRODUCTION

Migration of hydrogen atoms along the carbon skeleton in ionized hydrocarbon molecules has been proposed to account for the appearance of such fragments as CH_4^+ in the mass spectrum of propane and CH_3^+ in the spectrum of cyclohexane. These peaks can not be accounted for by isotopic contributions from C^{13}. Evidence for rearrangement of hydrogens prior to dissociation of the corresponding molecule ions has been reported by several workers (1, 2, 8). Some migration of deuterium atoms is reported in a recent paper on the mass spectra of deuterated butanes (5). Migration of atoms and isomerization of ionized molecules has been referred to by McDowell (4) in an interpretation of mass spectra based on excited molecular states. Processes of this type are of special interest because of the insight they provide into the nature of bonding forces in molecular ionic states.

The present study of the mass spectrum of 1-butene-4-d_3 arose in connection with mass spectral analysis of the pyrolysis products of this compound and of the light isomer 1-butene.

EXPERIMENTAL

The 1-butene used for purposes of comparison was Research Grade (99.88%) obtained from the Phillips Petroleum Company, Bartlesville, Okla. The deuterated butene was kindly prepared for us by Dr. L. C. Leitch of the National Research Laboratories, Ottawa, according to the following method:

$$CCl_3Br + CH_2{=}CH{-}CH_2Cl \xrightarrow{h\nu} CCl_3CH_2{-}CHBr{-}CH_2Cl,$$

$$CCl_3CH_2CHBrCH_2Cl \xrightarrow{Zn} CD_3CH_2CH{=}CH_2.$$

[1]*Manuscript received June 1, 1956.*
Contribution from the Department of Chemistry, The University of British Columbia, Vancouver, B.C.
[2]*This work was done under Defence Research Board Grant 5001-10 Project No. D44-50-01-10.*

The product was shown by analysis to be almost 100% C=C hydrocarbon. A preliminary mass spectrometric analysis using 10 volt electrons gave an uncertain result but indicated that the sample was better than 90% 1-butene-4-d_3. Conclusive proof of the purity of the compound was obtained by analysis with a Varian high resolution nuclear magnetic resonance (NMR) spectrometer. The NMR spectrum of the 1-butene is shown in Fig. 1(*a*). The peaks labelled *a*, *b*, *c*, and *d* are proton resonance absorption peaks for the hydrogens located on the carbons as follows:

$$\underset{a}{CH_2}{=}\underset{b}{CH}{-}\underset{c}{CH_2}{-}\underset{d}{CH_3}$$

The theoretical relative intensities of the two groups of peaks for 1-butene can be expressed as

$$(a+b)/(c+d) = (2+1)/(2+3) = 3/5.$$

The actual ratio found by measuring the area under the peaks was 3/5.8.

Fig. 1(*b*) shows the NMR spectrum of the deuterated butene. The identity

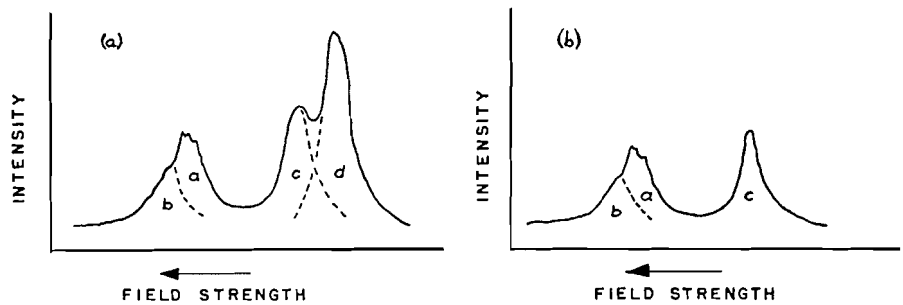

FIG. 1. (*a*) NMR absorption spectrum of $CH_3CH_2CH{=}CH_2$. (*b*) NMR absorption spectrum of $CD_3CH_2CH{=}CH_2$.

of the *a* and *b* peaks with those shown in Fig. 1(*a*) is obvious. The *d* peak of the CH_3 group in 1-butene has completely disappeared in the deuterated compound.

Deuterium atoms, having an even number of nucleons, do not exhibit NMR absorption. The relative intensities of the groups in

$$\underset{a}{CH_2}{=}\underset{b}{CH}{-}\underset{c}{CH_2}{-}\underset{d}{CD_3}$$

should be

$$(a+b)/(c+d) = (2+1)/(2+0) = 3/2.$$

The observed ratio was 3/2.26. The complete absence of a '*d*' branch in the spectrum of the deuterated compound was taken as conclusive evidence that the methyl group was completely deuterated, within the sensitivity of detection of the analytical method. The relative intensities of the *a*, *b*, and *c* branches demonstrate the absence of deuterium in the groups to which these peaks correspond.

As a check on the results obtained by NMR a comparison of the infrared

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spectra of the two butenes was made using a Perkin-Elmer double beam spectrophotometer. A complete interpretation of the spectra obtained has not yet been achieved but a preliminary band assignment confirms the results obtained by NMR.

The mass spectrum of the light butene is presented in Fig. 2 and that of the deuterated compound in Fig. 3. Fifty-volt electrons were used in obtaining

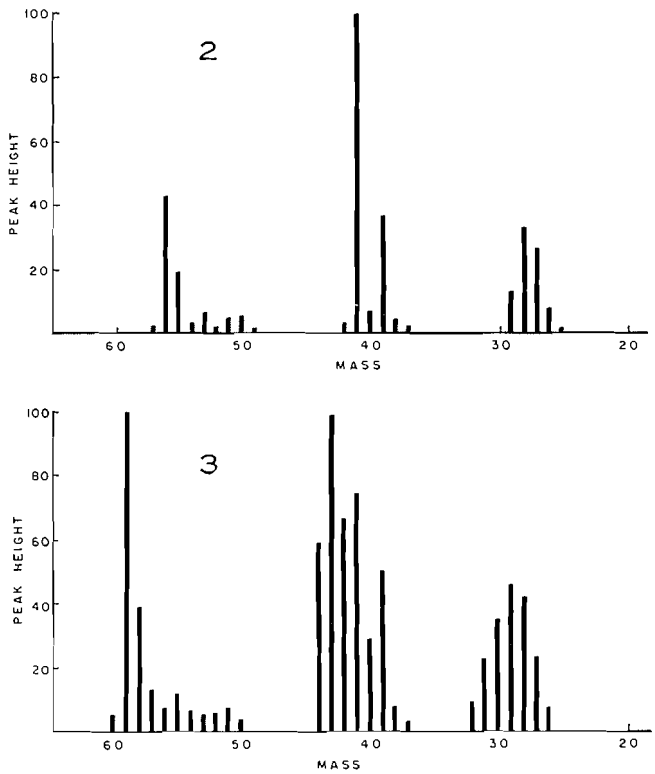

FIG. 2. Mass spectrum of $CH_3CH_2CH{=}CH_2$.
FIG. 3. Mass spectrum of $CD_3CH_2CH{=}CH_2$.

these spectra. The intensity of the largest peak in each spectrum is assigned a value of 100 in the usual way. Normalized spectra for both compounds are presented in Fig. 4. Here the total ion intensities for the C_4, C_3, C_2, and C_1 groups of ions are plotted on a scale such that the C_4 ion intensities are made equal. The solid peaks are for the undeuterated compound.

A detailed study of the fragmentation pattern of the deuterated butene at low electron energies was not made but a few preliminary results showing the intensities of various fragments as a function of electron energy are presented in Table I. The relative intensities at 50 electron volts are also shown.

Results obtained for the pyrolysis of the two butenes provided an interesting basis for comparison of the thermal and electron-impact modes of dissociation. The results given in Table II show the distribution of the principal products

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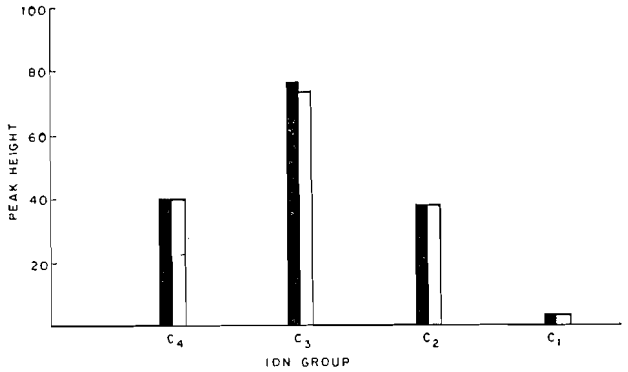

FIG. 4. Normalized spectra of $CH_3CH_2CH{=}CH_2$ (black) and $CD_3CH_2CH{=}CH_2$ (white) showing the relative total intensities for each group of ions.

TABLE I

VARIATION OF C_3 ION INTENSITY WITH ELECTRON ACCELERATING POTENTIAL FOR $CD_3CH_2CHCH_2$

Electron accelerating potential (volts)	Ion intensity (arbitrary units)			
	41	42	43	44
13.0	1.0	3.0	5.0	2.0
15.0	4.0	8.0	14.0	6.0
17.0	12.0	20.5	32.0	16.0
50.0	74.3	67.0	99.3	59.0

TABLE II

PYROLYSIS PRODUCTS FOR THE TWO BUTENES AFTER 5.0 MIN. AT 552°C.

	$CH_3CH_2CHCH_2$ (vol. %)	$CD_3CH_2CHCH_2$ (vol. %)
Methane	24.0	24.0
Ethane	5.3	5.2
Ethylene	8.3	9.0
Propylene	13.0	13.6

for the pyrolysis of 100 mm. of each hydrocarbon in a static system for 5 min. at 552°C. The analyses were performed by gas chromatography, using both adsorption-elution and partition-elution methods.

DISCUSSION

The mass spectrum of the light butene shows clearly that the most abundant fragment produced by electron impact is the $C_3H_5^+$ ion, formed presumably as a consequence of the preferred rupture of the $CH_3{-}CH_2CHCH_3$ bond. This ion would be expected to have the allyl structure, $CH_2C\overset{+}{H}CH_2$, but by rearrangement could assume structures such as $CH_2CH_2\overset{+}{C}H$ or $CH_3CH_2\overset{+}{C}$. A $C_3H_3^+$ fragment is also relatively abundant. The spectrum of the deuterated compound is markedly different from that of the light isotopic molecule. The chief difference is seen in the C_3 group of peaks. The $C_3H_5^+$ ion (mass 41),

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which might well be expected to be the most abundant 3-carbon fragment, accounts for only 19% of the total ion intensity. The greater part of the C_3 ion intensity comes from higher masses. Several possible formulas can be written for each of these ions, but the contributions of some of these to the ionic intensities will be negligible. Since the 42 peak from 1-butene is only slightly greater than the C^{13} isotopic peak the contribution of ions equivalent to $C_3H_6^+$ can be neglected. This includes ions such as $C_3H_4D_2^+$ (mass 44) and C_3H_5D (mass 43). In addition since the mass 40 peak from 1-butene is quite small, ions equivalent to $C_3H_4^+$ will make relatively small contributions to the low energy spectrum. Therefore, ions $C_3HD_3^+$ (mass 43), $C_3D_3^+$ (mass 42), and $C_3HD_2^+$ (mass 41) can be neglected. Thus, the greater part of the C_3 ion intensity comes from $C_3H_2D_3^+$ (mass 44), $C_3H_3D_2^+$ (mass 43), $C_3H_4D^+$ (mass 42), and $C_3H_5^+$ (mass 41). It is therefore apparent that migration of the deuterium atoms from the CD_3 group to the rest of the carbon skeleton must have occurred. Rearrangement of hydrogen atoms similar to the rearrangements observed in the deuterated butene will, of course, occur in the light compound but cannot be detected by the present method.

The relative intensities of the ions of masses 41 to 44 (Table I) provide some insight into the relationship between the energy of the ionizing electron and the extent of the migration process. At the lowest electron energy the $C_3H_5^+$ ion makes a comparatively small contribution to the total C_3 ion intensity. The contribution increases markedly with increasing electron energy. This can be seen from Table III in which the variation of the $C_3H_4D^+$ (42)+ $C_3H_3D_2^+$ (43) + $C_3H_2D_3^+$ (44) to $C_3H_5^+$ (41) intensity ratio is presented as a function of electron accelerating potential. It is apparent that deuterium migration is the less probable the higher the energy of the ionizing electron, a consequence presumably of the shorter lifetimes of ions in higher energy states. At lower electron energies the lifetimes of the ions are sufficient, perhaps several vibrations long, to permit extensive rearrangement of the atoms attached to the carbon skeleton.

TABLE III

VARIATION OF RATIO OF THE SUM OF MASSES 42, 43, AND 44 TO MASS 41 WITH ELECTRON ENERGY

Electron accelerating potential (volts)	$\frac{42+43+44}{41}$
13.0	10.0
15.0	7.0
17.0	5.7
50.0	3.0

The relative intensities of the ions of masses 42, 43, and 44 remain approximately constant for all electron energies. This indicates that the migration mechanism does not depend on the energy of the ionizing electron but is the same for all energies once ionization of the molecule has occurred. The factor controlling the extent of migration is the lifetime of the ion, as suggested above.

It can be seen from Fig. 4 that the total intensities of the ions of a given

carbon-number group are the same in the two butenes even though the distribution of intensities and the numbers of fragments observed within the groups are different. This similarity in group intensities shows that deuteration does not have any appreciable effect on the probability of C—C bond rupture. A similar lack of effect in the thermal decomposition of the parent molecule is shown by the distribution of pyrolysis products for the two isotopic compounds given in Table II.

The present work confirms the results reported by Stevenson and Wagner (8) and bears out their prediction that rearrangement of H and D atoms would be more extensive in olefinic than in paraffinic hydrocarbons. This is presumably a consequence of the less localized character of the bonding in the olefinic parent molecule-ion.

The variety of three-carbon fragments formed is evidence of the existence of a number of different modes of decomposition of the ionized molecules. The existence of such modes has been referred to by Rosenstock *et al.* (7) in attempting to calculate the mass spectra of polyatomic molecules from a statistical basis. Migration of deuterium atoms, with the resulting changes in configuration, results in transitions between various close-lying energy levels of the given ionic state. Such transitions are equivalent to the crossing of the corresponding potential energy surfaces. The over-all decomposition pattern of the molecule-ions will depend on the distribution of the ions among the various accessible energy states. Information is not yet available to permit the evaluation of the probabilities of the transitions referred to above. Lennard-Jones and Hall (3) have considered the probability of excitation to various electron states in *n*-octane by calculating the density of positive charge over the octane ion but little is known about the probability of transition between close-lying configurational states in polyatomic molecules.

The extensive migration of isotopic hydrogens observed in the present work casts some doubt on the reliability of the "fragmentation indices" calculated by Magat and Viallard (6) to describe the probability of bond rupture in the dissociation of hydrocarbons by electron impact. The necessity for caution in interpreting the results of mass spectral analyses where deuterium migration can occur is obvious.

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STRUCTURE OF A SYNTHETIC POLYXYLOSE[1]

By C. T. Bishop

ABSTRACT

D-Xylose has been condensed under the catalytic action of hydrogen chloride to yield 5.6% polyxylose having a number average degree of polymerization (D.P.) of 10 or greater. The polyxylose was shown to be highly branched with a predominance of the glycosidic bonds in the α-configuration. Estimation and identification of the hydrolysis products of the methylated polyxylose showed that the glycosidic linkages 1→4: 1→2: 1→3 occurred in a frequency ratio of 6.5: 3: 1.

In the presence of an acid catalyst monosaccharides may condense to form reversion products and there are many reports about the preparation and structures of low molecular weight oligosaccharides, mainly disaccharides, thus formed (11, 17, 19, 20, 22). There are a limited number of references to higher molecular weight polysaccharides, having a degree of polymerization (D.P.) greater than 10, formed by reversion. Pacsu and Mora (12) reported the isolation of a polyglucose having a D.P. of 37–42 and claimed that similar products could be obtained from D-mannose, D-fructose, L-arabinose, maltose, and cellobiose. However, no details were given of the polysaccharides formed from these latter sugars. Preparation of these polymers was accomplished by low temperature evaporation of a concentrated solution of the monosaccharide in 5% hydrochloric acid. Kent (8) has synthesized glucose polymers by heating glucose monohydrate with thionyl chloride and Theobald and Twigg (18) also used this method. Ricketts (14, 15) improved on these methods of polysaccharide syntheses by allowing crystalline D-glucose or its monohydrate to deliquesce in the presence of hydrogen chloride. It was postulated that by this process, the molecules of D-glucose, which in the crystalline state are as near to each other as possible, must pass through the optimum distance for bond formation as they dissolve.

The linkages formed in the reversion of hexoses by acid in the experiments just summarized were primarily 1→6 and were predominantly in the α-configuration. Of the glycosidic linkages other than 1→6, the 1→4 was prevalent but there was a notable absence of the 1→3. Since the final composition of a system undergoing acid reversion is determined by equilibria between hydrolytic and condensation reactions, the preferential occurrence of 1→6 over 1→4 over 1→3 linkages could be caused by (*a*) differences in acid-stability of the linkages once formed or (*b*) differences in reactivities of hydroxyl groups. There is evidence in favor of both effects: (*a*) Wolfrom *et al.* (24) showed that for glucose disaccharides the α, 1→4 linkage is hydrolyzed by acid four times as rapidly as the α, 1→6 bond, and Ricketts and Rowe (15) found that maltose is not incorporated as such into a polyglucose on acid reversion but yields a product very similar to that obtained from glucose, with a predominance of

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1→6 links. (*b*) It is known that under the conditions of acid reversion, high sugar concentrations, and low temperatures, di- and oligo-saccharides accumulate. The equilibrium hydrolysis⇄condensation must then be shifted towards the right and it would be expected that reactivities of the hydroxyl groups would determine the location of the glycosidic bonds. In this regard it should be noted that the frequency of occurrence of specific glycosidic bonds in reversion products agrees with the differences in reactivities of the hydroxyl groups as determined by other means (16). Therefore, in acid reversion of hexoses, since both viewpoints (*a*) and (*b*) lead to the same result, it appears that the most stable linkages are formed at the most reactive hydroxyl groups. There is little quantitative data on the different glycosidic bonds formed in reversion of sugars, particularly those formed at secondary hydroxyl groups. The problem is difficult in the hexose series where the great preponderance of 1→6 linkages interferes, but the difficulty could be overcome by using a pentose which, in its stable pyranose form, has no primary hydroxyls. This idea led to a study of the polymerization of D-xylose and estimation of the frequency of occurrence of different glycosidic linkages in the polymer by classical methylation techniques as reported here.

D-Xylose was polymerized under the same conditions used by Ricketts (14) for preparing a polyglucose. Extraction of the dried non-dialyzable material from this condensation with different concentrations of ethanol yielded the three fractions listed in Table I. The 5.6% yield of polyxylose having a D.P.

TABLE I

SYNTHETIC XYLANS

Fraction	Yield	$[\alpha]_D^{25}$ (c = 2 in water)	Degree of polymerization
1	1.32 gm. (2.64%)	+93°±1°	7
2	1.11 gm. (2.24%)	+88°±1°	10
3	1.69 gm. (3.38%)	+55°±2°	15

of 10 or greater was low in comparison with that obtained from glucose, 17–45% (14, 15), and was undoubtedly caused by decomposition of D-xylose under the strong acidic conditions. The D.P. values given are number averages, having been determined by hypoiodite oxidation, and hence represent the repeating unit of the polyxylose. The actual particle size may, of course, be much larger. The high positive rotations of the products showed that the glycosidic linkages were predominantly in the α-configuration but the decrease in rotation with increasing D.P. would indicate the presence of some β-linkages. This is in agreement with the results of Thompson *et al.* (19) who found both α- and β-links in reversion products of D-glucose. When oxidized by periodate, Fractions 1, 2, and 3 respectively consumed 1.22, 0.97, and 0.97 moles of oxidant per mole anhydro-D-xylose with the concurrent release of 0.85, 0.50, and 0.40 moles of formic acid per mole anhydro-D-xylose. Fraction 1 was obviously overoxidized but the results for Fractions 2 and 3 were indicative of highly branched polyxyloses containing 3–4 non-reducing terminal xylose units.

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Fraction 3 was methylated and hydrolyzed to yield the methyl ethers of D-xylose shown in Table II. These compounds were separated by partition on

TABLE II

COLUMN CHROMATOGRAPHIC SEPARATION OF HYDROLYSIS PRODUCTS OF METHYLATED SYNTHETIC POLYXYLOSE

Receiver number	Component	Chromatographic identity	Yield, mgm. (mM.)	$[\alpha]_D^{25}$ (c = 1% in water)
96–125	1	2,3,4-Tri-*O*-methyl-D-xylose	214 (1.1)	+19°±2°
130–169	2	2,3-Di-*O*-methyl-D-xylose	441 (2.5)	+22°±2°
170–200	3	2,4-Di-*O*-methyl-D-xylose	66 (0.37)	+22°±2°
220–360	4	3-*O*-Methyl-D-xylose	285 (1.7)	+18°±2°
379–564	5	D-Xylose	82 (0.55)	+17°±2°
			1088 mgm. = 94.8% recovery	

Celite columns (9) and were identified by isolation of crystalline products. The quantities of these hydrolysis products were in the following approximate molar relationship: 2,3,4-tri-*O*-methyl-D-xylose (3 moles); 2,3-di-*O*-methyl-D-xylose (7 moles); 2,4-di-*O*-methyl-D-xylose (1 mole); 3-*O*-methyl-D-xylose (5 moles); and D-xylose (1 mole). These results confirmed the branched structure predicted by periodate oxidation, and the total number of moles, 17, being an approximation to the nearest whole number is in good agreement with the number average D.P. of 15 determined by hypoiodite oxidation. If the reversion is regarded as a hydrolysis⇄condensation equilibrium then pyranose ring forms should accumulate in the polymer as the less acid-stable furanoside linkages are hydrolyzed, and in the polyglucose formed by acid reversion no infrared absorption associated with furanoside rings was detected (15). Making the reasonable assumption then that the D-xylose units are in the pyranose form, the methylation results showed the presence of thirteen 1→4 links, six 1→2 links, and two 1→3 links in the polyxylose. This gives a frequency ratio for 1→4 : 1→2 : 1→3 of 6.5:3:1. Whether the most stable linkages are formed at the most reactive hydroxyls in D-xylose as in D-glucose is not known yet but the results given here are in agreement with the greater reactivity of the 2 and 4 positions as compared with 3 in D-xylose as determined by partial methylation (1). An estimate of the stabilities of the linkages will require measurement of the relative rates of hydrolysis of xylose disaccharides having 1→2, 1→3, and 1→4 glycosidic bonds.

EXPERIMENTAL

Chromatographic separations on paper strips were carried out in the following solvent systems (v/v): (A) pyridine: ethyl acetate: water—1:2:2, (B) *n*-butanol: ethanol: water—5:1:4, and (C) *n*-butanol saturated with water. Sugars were detected on the papers by silver nitrate (21) and aniline oxalate (7) spray reagents. Evaporations were done at 40° C. or less, and specific rotations are equilibrium values unless otherwise stated. Melting points are corrected.

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Preparation of Polysaccharide

Crystalline D-xylose (50 gm.) was spread in a fine layer in a crystallizing dish and allowed to stand for seven days in a closed desiccator over concentrated hydrochloric acid (50 ml.) to which 10 drops of concentrated sulphuric acid had been added (14). The dark sirupy product was stirred into crushed ice and the acid was neutralized with 10% sodium hydroxide. The neutral solution was dialyzed in a cellophane membrane against running, distilled water for 24 hr. Evaporation of the non-dialyzable mixture to dryness, followed by successive, exhaustive extractions of the residue with 100%, 85%, and 75% aqueous ethanol, yielded Fractions 1, 2, and 3 respectively. Further extraction of the residue with more dilute ethanol (e.g. 65%) removed products contaminated with colored impurities formed during the condensation, so no more fractions were isolated. Ethanol was evaporated from each fraction, and aqueous solutions of the residues were freeze-dried yielding white, fluffy powders. Table I shows the yields, specific rotations, and degrees of polymerization determined by hypoiodite oxidation (6) of the three fractions. When the three fractions were hydrolyzed by *N* hydrochloric acid at 97° C., their specific rotations changed in four hours to a constant value of $+19°\pm1°$, equal to that of D-xylose, and xylose was the only sugar detectable by paper strip chromatography (Solvent A).

Periodate Oxidations

Samples (2.03 mgm., 0.0154 mM.) of each fraction were oxidized by periodate at pH 5.7 and 20° C. using the Warburg respirometer for continuous measurement of formic acid production (13). Amounts of periodate consumed were determined, after formic acid production was constant, by the usual excess arsenite method (4, 5). In 65 hr., production of formic acid reached constant values of 0.85, 0.50, and 0.40 moles per mole anhydro-D-xylose unit for Fractions 1, 2, and 3 respectively. Periodate consumptions by these three fractions at the same time and in the same sequence were 1.22, 0.97, and 0.97 moles per mole anhydro-D-xylose unit.

Methylation

Fraction 3 (8.66 gm.) was suspended in tetrahydrofuran (250 ml.) and solid sodium hydroxide pellets (30 gm.) were added. The mixture was stirred vigorously during the dropwise addition of dimethyl sulphate (40 ml.) over an eight hour period and stirring was continued for a further 18 hr. The mixture was then heated to 70° C. and enough water was added to dissolve the inorganic salts. Tetrahydrofuran was removed by evaporation and the residual aqueous solution was cooled to 0° C. before addition of 10% sulphuric acid to pH 8. Sodium sulphate which precipitated was filtered and washed with chloroform and the aqueous filtrate was extracted four times with an equal volume of fresh chloroform. The combined chloroform extracts were dried over anhydrous sodium sulphate and evaporated to a sirup (6.25 gm., $OCH_3 = 34.6\%$). This product was remethylated as just described but the product was isolated this time by continuous extraction of the aqueous solution (pH 8) for 18 hr. with chloroform. The product (4.80 gm.) was a friable solid having no hydroxyl absorption peak at 3400 $cm.^{-1}$ in its infrared spectrum; $[\alpha]_D^{25} = +65°\pm2°$

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(c = 0.8% in chloroform). Analysis: Calc. for $C_8H_{15}O_4[C_7H_{12}O_4]_{13}.C_8H_{15}O_5$ ($32\times OCH_3$): OCH_3, 40.5%. Found: OCH_3, 41.8%.

Hydrolysis of Methylated Xylan

The methylated polysaccharide (4.77 gm.) was dissolved in 5% methanolic hydrogen chloride (200 ml.) and the solution was refluxed till it reached a constant rotation (10 hr.). Methanol was evaporated at 37° C. and *N* hydrochloric acid (100 ml.) was added to the residue. This mixture was then heated on a boiling water bath for seven hours after which the acid was removed by Dowex-2 ion exchange resin (carbonate form). The neutral solution was evaporated to a sirup (3.6 gm.) which qualitative paper strip chromatography in Solvents B and C showed was a mixture of a tri-*O*-methyl xylose, two di-*O*-methyl xyloses, an *O*-methyl xylose, and xylose. By running authentic samples on the same paper strip these components were chromatographically identified as xylose and its following methyl ethers: 2,3,4-tri-*O*-methyl; 2,3-di-*O*-methyl; 2,4-di-*O*-methyl; and 3-*O*-methyl.

Separation of Hydrolysis Products

A portion (1.1 gm.) of the mixture of components from hydrolysis of the methylated xylan was resolved by partition on a Celite No. 535 column (295 gm., 50×5 cm.) using water-saturated *n*-butanol as the developing solvent (9). The separation was carried out by the elution technique and fractions of 7.5 ml. were collected by an automatic device which changed the receiver every three minutes. Every fifth tube was examined by paper strip chromatography (Solvent B) to give a picture of the distribution of sugars, and it was found that a complete separation of each component had been obtained. The portions of eluate containing the individual sugars were evaporated and the residues were redissolved in water. These solutions were then clarified by filtration and evaporated to sirups which were dried to constant weight at 0.02 mm. over phosphoric anhydride. Table II shows the results of the separation.

Identification of Hydrolysis Products

Component 1 had $[\alpha]_D^{25} = +19°\pm2°$ (c = 1% in water) and was chromatographically identical with 2,3,4-tri-*O*-methyl-D-xylose in Solvent B. The sirup crystallized completely after being kept for two days in a desiccator at room temperature and recrystallization from ether yielded 2,3,4-tri-*O*-methyl-D-xylose, m.p. and mixed m.p. 91–92° C., $[\alpha]_D^{27} = +22°\pm2°$ (c = 2% in water); reported (2): m.p. 87–90° C., $[\alpha]_D^{25} = +20°$ (c = 1.5% in water).

Component 2 was a sirup having the same R_f value as 2,3-di-*O*-methyl-D-xylose in Solvent B and $[\alpha]_D^{25} = +22°\pm2°$ (c = 1% in water). The sugar (50 mgm.) was refluxed for three hours with 1.5 moles of aniline in absolute ethanol (2.0 ml.). The solution was evaporated to a sirup which crystallized after nucleation with the anilide of 2,3-di-*O*-methyl-D-xylose (m.p. 124–125° C.). Recrystallization from ethyl acetate yielded 2,3-di-*O*-methyl-*N*-phenyl-D-xylopyranosylamine, m.p. and mixed m.p. 124–125° C., $[\alpha]_D^{27} = +185°\pm5°$ (c = 0.4% in ethyl acetate; reported (3): m.p. 126° C., $[\alpha]_D^{25} = +180°$ (in ethyl acetate).

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Component 3, $[\alpha]_D^{25} = +22° \pm 2°$ ($c = 1\%$ in water), was identical with 2,4-di-*O*-methyl-D-xylose on paper chromatograms (Solvent B) and crystallized spontaneously when an aqueous solution of it was evaporated to dryness. Recrystallized from ethyl acetate, the compound had m.p. 110–111° C., unchanged on admixture with an authentic sample of 2,4-di-*O*-methyl-D-xylose, and $[\alpha]_D^{27} = +22° \pm 2°$ ($c = 1.1\%$ in water); reported (1): m.p. 108° C., $[\alpha]_D^{20} = +22°$ (in water).

Component 4 had $[\alpha]_D^{25} = +18° \pm 2°$ ($c = 1\%$ in water) and ran the same as 3-*O*-methyl-D-xylose on chromatograms (Solvents B and C). The sirup was nucleated with an authentic sample of 3-*O*-methyl-D-xylose after which it crystallized slowly over a two-week period. The product, recrystallized from acetone, had m.p. and mixed m.p. 102–103° C. and $[\alpha]_D^{27} = +18° \pm 1°$ ($c = 3.8\%$ in water); reported (10): m.p. 102–103.5° C., $[\alpha]_D^{22} = +17.2°$ ($c = 2\%$ in water).

Component 5, $[\alpha]_D^{25} = +17° \pm 2$ ($c = 1\%$ in water), was chromatographically identical with D-xylose (Solvents A and B) and the sirup crystallized spontaneously. Recrystallization from glacial acetic acid yielded D-xylose, m.p. and mixed m.p. 145–146° C., $[\alpha]_D^{27} = +18° \pm 1°$ ($c = 3.2\%$ in water); reported (23): m.p. 144–145° C., $[\alpha]_D^{22} = +18.5°$ ($c = 10\%$ in water).

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THIAZOLES

II. PREPARATION OF ALKYL-2-NITRAMINOTHIAZOLES[1,2]

By Sidney Kasman[3] and Alfred Taurins

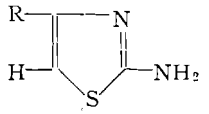
ABSTRACT

1-Chloro-3-methyl-2-butanone and 2-amino-4-*iso*propylthiazole have been synthesized. The mononitration of 2-aminothiazole and five alkyl-2-aminothiazoles in the 2-amino group has been carried out with absolute nitric acid in concentrated sulphuric acid at low temperatures ranging from 0° to −10°. 2-Nitramino- and alkyl-2-nitramino-thiazoles are crystalline, stable compounds. The dinitration of some alkyl-2-aminothiazoles under the same conditions lead to the formation of alkyl-2-nitramino-5-nitrothiazoles. The rearrangement of 2-nitraminothiazole to 2-amino-5-nitrothiazole was studied in the presence of mesitylene for the first time.

A previous paper (10) of this laboratory described the further nitration of 2-nitramino-5-nitrothiazole with a mixture of 99–100% nitric acid in acetic anhydride. In the same article a summary of previous investigations on the exceptional formation of the dinitration products was given.

The objective of this work was to study the nitration of 2-aminothiazole and several alkyl-2-aminothiazoles under conditions at which the nitration would occur only in the amino group without substituting the hydrogen in the 5-position. The nitrating agent used was absolute nitric acid and the reaction medium was concentrated sulphuric acid. After the completion of this investigation (8) a paper by Dickey, Towne, and Wright (2) appeared dealing partly with the same problem. These authors nitrated 2-aminothiazole in systems containing up to 30% water.

We expected that selective mononitration of the 2-amino group would be favored by the use of a limited quantity of nitric acid, by short reaction time, and by low reaction temperature. The addition of nitric acid to the 2-aminothiazole (I), instead of the reverse, should also foster mononitration through the absence of an excess of nitric acid. It was soon found that one or two excess equivalents of nitric acid were not harmful and increased the yields, that reaction times of the order of a few minutes to an hour were satisfactory, and that the critical factor was the reaction temperature. The working region was found to lie between −10° and 0°.



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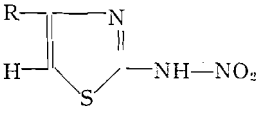
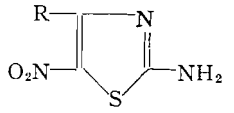
IV: R = CH_3
VII: R = C_2H_5
X: R = *i*-C_3H_7



II: R = H
V: R = CH_3
VIII: R = C_2H_5
XI: R = *i*-C_3H_7



III: R = H
VI: R = CH_3
IX: R = C_2H_5
XII: R = *i*-C_3H_7

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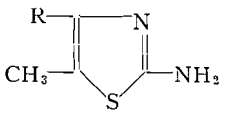
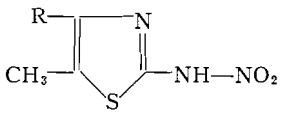
[2]*Part I of this series by S. J. Viron and A. Taurins, Can. J. Chem. 31: 885. 1953.*

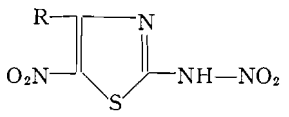
[3]*Holder of a Canadian Industries (1954) Limited Scholarship, 1953–1954.*



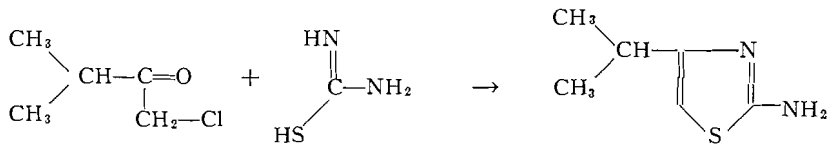
XIII: R = H
XV: R = CH_3



XIV: R = H
XVI: R = CH_3



XVII: R = CH_3
XVIII: R = i-C_3H_7



XIX X

Solutions obtained in this way by the nitration of 2-aminothiazole were invariably found to precipitate a product when poured onto ice. After purification, it was demonstrated to be 2-nitraminothiazole (II) unnitrated in the ring. The 2-nitraminothiazole was found to be a nearly white crystalline solid, acidic to litmus, slightly soluble in water, and quite soluble in dilute sodium hydroxide solution, from which it precipitated on acidification. It gave a positive Franchimont test (5) and deflagrated or exploded when heated to the melting point. The 2-nitraminothiazole was always accompanied by a small amount of 2-amino-5-nitrothiazole (III). This coproduct was precipitated from the acid filtrate by treatment with excess alkali.

The method described for the preparation of 2-nitraminothiazole was found to be applicable to a number of alkyl-substituted thiazoles. At first, 2-amino-4-methylthiazole (IV) (3) was mononitrated to 4-methyl-2-nitraminothiazole (V) in cold sulphuric acid using one equivalent of nitric acid. The reaction was quenched after 15 min. to obtain 56% yield of (V) and 40% of 2-amino-4-methyl-5-nitrothiazole (VI). Lower reaction temperatures favored the formation of the nitramine (V), while higher temperatures favored the formation of the 5-nitro compound (VI).

The next homologous compound, 2-amino-4-ethylthiazole (VII) (9), was nitrated by the same method for 15 min. The unreacted nitric acid was destroyed with absolute alcohol and the reaction was quenched on ice. The yield of 4-ethyl-2-nitraminothiazole (VIII) was 42%, and of 2-amino-4-ethyl-5-nitrothiazole (IX), 4.8%. In another experiment the reaction mixture was stirred for one hour before quenching the reaction. No nitramine could then be isolated, but a 68% yield of (IX) was obtained. These two nitration experiments demonstrated the rearrangement of the nitramine (VIII) into amino-nitro compound (IX), and its importance in the formation of 2-amino-5-nitrothiazoles.

We synthesized for the first time 2-amino-4-*iso*propylthiazole (X) by condensing 1-chloro-3-methyl-2-butanone with thiourea. The 1-chloro-3-methyl-2-butanone (XIX) was prepared in 38% yield by the action of diazomethane on 2-methylpropionyl chloride, followed by treatment with dry hydrogen

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chloride. Mononitration of 2-amino-4-*iso*propylthiazole (X) in cold sulphuric acid gave a 37% yield of pure 4-*iso*propyl-2-nitraminothiazole (XI) and a 32% yield of 2-amino-4-*iso*propyl-5-nitrothiazole (XII).

As an example of a 2-amino-5-alkylthiazole, 2-amino-5-methylthiazole (XIII) gave on nitration, at best, a 22% yield of 5-methyl-2-nitraminothiazole (XIV) when the unreacted nitric acid was destroyed with alcohol. The mononitration of 2-amino-4,5-dimethylthiazole (XV) (4, 7) tended to give gummy products, but a small amount of 4,5-dimethyl-2-nitraminothiazole (XVI) was isolated.

Dinitration

The dinitration of two 2-amino-4-alkylthiazoles was carried out in concentrated sulphuric acid at low temperature using 2.2 to 2.4 equivalents of absolute nitric acid. The nitration of 2-amino-4-methylthiazole (IV) gave a 41% yield of pure 4-methyl-2-nitramino-5-nitrothiazole (XVII) and a 34% yield of 2-amino-4-methyl-5-nitrothiazole (VI). Under similar conditions 2-amino-4-*iso*propylthiazole (X) gave 2-nitramino-5-nitro-4-*iso*propylthiazole (XVIII) (45% yield), which was accompanied by a 13% yield of 2-amino-4-*iso*propyl-5-nitrothiazole (XII).

Rates of Nitration

In order to compare qualitatively the rates of nitration of the 2-amino group and hydrogen atom in the 5-position, a sample of 2-aminothiazole was nitrated at −5° and aliquots of the cold reaction mixture were withdrawn 7 and 67 min. after the addition of nitric acid was completed. After removal, these two aliquots were promptly quenched on ice. The precipitated 2-nitraminothiazole (II) was filtered off and crystallized from 95% ethanol. The yields were corrected for solubility in cold 95% ethanol (0.55 gm./100 ml.). The acid filtrates were rendered alkaline and the precipitated 2-amino-5-nitrothiazole (III) was crystallized from 95% ethanol. The results are listed in Table I.

TABLE I

Aliquot	Yield of 2-nitraminothiazole(II)	Yield of 2-amino-5-nitrothiazole (III)
1	1.95 gm.; 37.4%	0.16 gm.; 3.1%
2	1.72 gm.; 33.0%	0.16 gm.; 3.1%
3	None	2.14 gm.; 52.7%

This experiment shows that at −5° the rate of formation of 2-nitraminothiazole is quite high and involves an equilibrium reaction. Under the same conditions the process which forms 2-amino-5-nitrothiazole does not proceed at a significant rate. The small initial yield of 2-amino-5-nitrothiazole must have been formed under conditions peculiar to the beginning of the reaction. Otherwise the yield of (III) would be expected to increase markedly in one hour over the 3% found after only seven minutes, since nuclear nitro groups are introduced in an irreversible reaction. Local heating was unavoidably

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produced during the dropwise addition of nitric acid solution to the reaction mixture. It was probably due to the exothermic nature of the nitration reaction and to the heat of dilution of nitric acid in sulphuric acid.

In another nitration, two equivalents of nitric acid were used, and 6.4% of 2-amino-5-nitrothiazole was isolated, supporting the view that transient high temperatures were responsible for the initial formation of this nitration product.

The residual solution, the third aliquot of the first batch, was warmed gently. Its temperature rose suddenly to 140° and then dropped rapidly. In this process all of the 2-nitraminothiazole, as well as some of the hitherto unreacted 2-aminothiazole, appeared in highly augmented yield (52.7%) of 2-amino-5-nitrothiazole. This result indicates the high activation energy and great temperature dependence of the nuclear nitration reaction.

Another pair of nitration experiments was carried out with 2-amino-4-ethylthiazole (VII) at temperature below 0°, with one equivalent of nitric acid. Five minutes after the nitric acid was added, 42% of 4-ethyl-2-nitraminothiazole (VIII) and 4.8% of 2-amino-4-ethyl-5-nitrothiazole (IX) were isolated. After 65 min. at 0°, only (IX) in 68% yield could be isolated. The +Is effect of the 4-ethyl group has undoubtedly activated the 5-position to nitronium ion attack, as compared with the 5-position of 2-aminothiazole. Nevertheless, the rate of nuclear nitration is still very slow compared with the rate of nitration of the 2-amino group. The final isolation of only 2-amino-4-ethyl-5-nitrothiazole is another example of a slow irreversible nuclear nitration reaction prevailing over a fast reversible nitration reaction of the amino group.

Rearrangement Experiments

The rearrangement of 2-nitraminothiazole to 2-amino-5-nitrothiazole when added to concentrated sulphuric acid was observed to proceed readily. The mechanism of the acid-catalyzed rearrangement of aromatic nitramines has not been extensively investigated, and some uncertainty remains in the interpretation of results. Bradfield and Orton (1) measured photometrically the rate of isomerization of 2-bromo-4-methyl-1-nitraminobenzene to 6-amino-2-bromo-4-methylnitrobenzene. Hughes and Jones (6) studied the rearrangement of nitraminobenzene in acidic medium in the presence of a foreign substance which can be easily nitrated. They added 1,4-dimethylbenzene, phenol, or dimethylaniline, which were nitrated by the rearranging nitramine. They found that the compounds mentioned above gave complicated nitration mixtures when used as the foreign substance.

We made a search for a compound which could be easily nitrated to yield only one mononitration product which would be steam-volatile for easy separation and solid for easy purification. We found that 1,3,5-trimethylbenzene (mesitylene) satisfied these criteria. To ensure the formation of only mononitromesitylene, *two* molar equivalents of mesitylene were suspended in stirred concentrated sulphuric acid at 0° and one molar equivalent of 2-nitraminothiazole was added in portions. From the diluted reaction mixture, an oily solid was separated by steam distillation. The solid was filtered from the oil which was reduced with tin and hydrochloric acid and acetylated with

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acetic anhydride. When it had been purified, the original solid proved, surprisingly, to be 2,4-dinitro-1,3,5-trimethylbenzene.

Since mesitylene was present in excess during the rearrangement and since a nitro group tends to deactivate an aromatic ring, it is difficult to account for the exclusive formation of dinitromesitylene. If nitromesitylene is much more soluble in sulphuric acid than mesitylene, it is understandable that the homogeneous reagent reacts more quickly than the heterogeneous one.

The nitration of added mesitylene leaves little doubt that in the rearrangement of 2-nitraminothiazole, an intermolecular mechanism is important.

EXPERIMENTAL

2-Nitraminothiazole (II)

(*a*) To 30 ml. of concentrated sulphuric acid was added 21.0 gm. (0.21 mole) of 2-aminothiazole (I) in portions, while stirring and cooling. The temperature was kept below 0° by intermittent cooling with a dry ice – alcohol bath. About 15 ml. of concentrated sulphuric acid was cooled to −30° and 9.2 ml. (13.9 gm., 0.22 mole) of absolute nitric acid was added to it. The mixture was stirred as it warmed up and became fluid. The mixed acid solution was added dropwise to the stirred amine sulphate mixture during 15 min. The reaction temperature was maintained at 0±3°. The solution was then stirred for 55 min. at 2–3° and poured onto 65 gm. of chipped ice. The resulting creamy precipitate was filtered off under suction and crystallized immediately from 300 ml. of 95% alcohol. The crystals were in the form of needles. The pure crystalline 2-nitraminothiazole (II) exploded at 204.7°. The yield was 7.2 gm. (23.7%).

A 0.1478 gm. sample of (II) required 10.95 ml. of 0.0926 *N* sodium hydroxide solution for neutralization. Equiv. wt. Calc. for $C_3H_3O_2N_3S$: 145.1. Found: 145.7. Anal. Calc. for $C_3H_3O_2N_3S$: C, 24.82; H, 2.08%. Found: C, 25.11; H, 2.29%.

(*b*) In another preparation, 5.00 gm. (0.05 mole) of (I) in sulphuric acid was nitrated with 4.17 ml. (6.30 gm., 0.10 mole) of nitric acid in sulphuric acid. The mixed acid was added during 55 min. while the reaction temperature was kept below 0°. After the nitric acid was added, stirring and cooling was continued for two min. and then 5 ml. of methanol was run in during eight minutes, while the temperature was kept below 0°. Stirring was continued for another two minutes and the reaction mixture was poured onto 25 gm. of chipped ice. The precipitated nitramine (II) was filtered off, boiled with 120 ml. of water and some active charcoal, and gravity filtered while hot. This yielded 3.21 gm. of pure dried product (44.3%), m.p. 204.7°. Rendered just alkaline with concentrated ammonia, the diluted sulphuric acid filtrate precipitated 0.56 gm. of 2-amino-5-nitrothiazole (III), which after crystallization from alcohol melted at 195°.

4-Methyl-2-nitraminothiazole (V)

To a stirred mixture of 11.4 gm. (0.10 mole) 2-amino-4-methylthiazole (IV) in 15 ml. of sulphuric acid cooled to −8° was added 4.35 ml. (6.61 gm., 0.105 mole) of nitric acid in 7 ml. of sulphuric acid during 50 min. The reaction mixture was then stirred five minutes at 5° and poured onto 35 gm. of chipped

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ice. The resulting sludgy precipitate was extracted with 150 ml. of boiling 95% alcohol and filtered while hot. The filtrate was reboiled with charcoal and filtered to give a deep red filtrate. The resulting matted needles were filtered off and the filtrate was reboiled and passed through the sludge again. A second crop of needles was obtained on cooling. The filtrate was reduced to 60 ml., cooled in ice, and diluted with 25 ml. of water. A third crop was obtained. The combined nitramine product weighed 8.96 gm. (56.4%) when dry. Crystallized from 10% acetic acid, 4-methyl-2-nitraminothiazole (V) melted at 190° with decomposition. Anal. Calc. for $C_4H_5O_2N_3S$: C, 30.18; H, 3.14%. Found: C, 30.27; H, 3.29%.

The dilute sulphuric acid filtrate yielded 6.32 gm. (39.8%) of 2-amino-4-methyl-5-nitrothiazole (VI). After two crystallizations from 50% alcohol, it melted at 218–219° with decomposition.

4-Ethyl-2-nitraminothiazole (VIII)

A solution of 0.83 ml. (1.26 gm.; 0.02 mole) nitric acid in 1 ml. of sulphuric acid was added to a stirred solution of 2.56 gm. of 2-amino-4-ethylthiazole (VII) in 5 ml. of sulphuric acid at −5° during five minutes. The mixture was stirred for five minutes below 0° and then poured onto 18 gm. of chipped ice. The precipitate of nitramine was crystallized from 150 ml. of 7% acetic acid to yield 1.46 gm. (42.1%) of pure 4-ethyl-2-nitraminothiazole (VIII), melting at 190° with decomposition. Anal. Calc. for $C_5H_7O_2N_3S$: C, 34.69; H, 4.08%. Found: C, 34.61; H, 3.96%.

The sulphuric acid filtrate was made alkaline with concentrated ammonia. The precipitate was filtered off and dried to obtain 0.27 gm. (4.8%) of 2-amino-4-ethyl-5-nitrothiazole (IX). After two crystallizations from 50% alcohol it melted at 197.5° with decomposition. Anal. Calc. for $C_5H_7O_2N_3S$: C, 34.69; H, 4.08%. Found: C, 34.83; H, 3.98%.

2-Methylpropionyl Chloride

A solution of 106 gm. (1.20 moles) of *iso*butyric acid and 161 gm. (1.35 moles) of thionyl chloride was heated under reflux for one hour and then slowly distilled. The product collected between 86° and 92° weighed about 150 gm. and was obviously contaminated with thionyl chloride. The product was refluxed for two hours with 15 gm. (0.12 mole) of benzoic acid and distilled. The procedure was carried out two more times, finally yielding 90.3 gm. (70.5%) of 2-methylpropionyl chloride, boiling at 92–94°.

1-Chloro-3-methyl-2-butanone (XIX)

Diazomethane was generated in the usual way from 100 gm. (0.97 mole) of nitrosomethylurea and dried over potassium hydroxide pellets. The solution was cooled with ice and stirred while 2-methylpropionyl chloride was added dropwise. The solution was allowed to stand for one hour at 5°. Dry hydrogen chloride was then bubbled through the solution for one hour and the ether was distilled off. The residual oil was distilled over at about 60 mm. pressure and then fractionally distilled at atmospheric pressure. The fraction boiling at

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149–152° weighed 17.48 gm. (38%). Attempts to prepare the oxime were unsuccessful. The pale yellow liquid had a specific gravity of 1.022 gm./cc. at 28° and a refractive index, n_D^{28} 1.4252. M_D Calc., 30.17. Found, 30.18.

2-Amino-4-isopropylthiazole (*X*)

A mixture of 16.25 gm. (0.135 mole) of 1-chloro-3-methyl-2-butanone, 10.7 gm. (0.140 mole) of thiourea, and 11 ml. of 95% alcohol was warmed under reflux on the steam bath. After a few minutes, a vigorous exothermic reaction occurred. Heating was continued for one hour under reflux and then the condenser was removed to permit alcohol to escape. The residue was made alkaline with concentrated ammonia, diluted with water, filtered to remove an insoluble scum, and extracted with three 35-ml. portions of ether. The extracts were dried over anhydrous magnesium sulphate and distilled to remove ether. The residue was distilled under vacuum to give a readily crystallizing pale yellow oil. Yield 14.88 gm. (77.5%), melting at 48–50°. Picrate: m.p. 216–217° decomp. Anal. Calc. for $C_{12}H_{23}O_7N_5S$: C, 38.83; H, 3.53%. Found: C, 38.96; H, 3.83%.

2-Acetamido-4-isopropylthiazole

A mixture of 1.42 gm. (0.01 mole) of 2-amino-4-*iso*propylthiazole and 3 ml. (3.24 gm., 0.03 mole) of acetic anhydride was warmed briefly on the steam bath to obtain a solution. After it had been left for four hours at room temperature, the solution was poured onto 5 gm. of chipped ice and the resulting white granular precipitate was filtered off and dried. It weighed 1.70 gm. (93.5%). One crystallization from 50% alcohol improved the melting point from 143–144° to 145.8–146.5°. Anal. Calc. for $C_8H_{12}ON_2S$: C, 52.16; H, 6.57%. Found: C, 52.37; H, 6.66%.

4-Isopropyl-2-nitraminothiazole (*XI*)

A solution of 1.45 ml. (2.20 gm., 0.035 mole) of nitric acid and 2 ml. of sulphuric acid was added during 14 min. to a stirred mixture of 4.26 gm. (0.03 mole) of 2-amino-4-isopropylthiazole (X) and 5 ml. of sulphuric acid at −25°. Stirring was continued for 10 min. at −20° and then an excess (2 ml.) of absolute alcohol was cautiously added at −15°. The reaction mixture was rinsed onto 30 gm. of supercooled, chipped ice and the resulting precipitate was filtered off and rinsed with alcohol. It was crystallized from 140 ml. of 50% alcohol to obtain 2.10 gm. (37%) of (XI) in the form of golden needles, melting at 185° with decomposition. Equiv. wt. Calc. for $C_6H_9O_2N_3S$: 187. Found: 184. Anal. Calc. for $C_6H_9O_2N_3S$: C, 38.50; H, 4.85%. Found: C, 38.22; H, 5.07%.

2-Amino-4-isopropyl-5-nitrothiazole (*XII*)

The dilute sulphuric acid filtrate was made alkaline with an excess of concentrated ammonia and the resulting precipitate of (XII) was filtered off and dried. Crude yield: 1.82 gm. (32.4%). After three crystallizations from 50% alcohol, a pure compound, melting at 230–231° with decomposition, was obtained. Anal. Calc. for $C_6H_9O_2N_3S$: C, 38.50; H, 4.85%. Found: C, 38.70; H, 4.80%.

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4-Isopropyl-2-nitramino-5-nitrothiazole (*XVIII*)

A solution of 4.00 ml. (6.04 gm., 0.096 mole) nitric acid in 3 ml. of sulphuric acid was added during seven minutes to a stirred mixture of 5.68 gm. (0.04 mole) 2-amino-4-*iso*propylthiazole (X) in 7 ml. sulphuric acid at −17°. The red solution was stirred for 1.2 hr. while immersed in an ice-water bath, which was then removed. The reaction temperature rose to 30° and was reduced by ice cooling. The mixture was then stirred for 4.7 hr. without cooling. An excess of absolute alcohol was added cautiously and the reaction mixture was poured onto 40 gm. of chipped ice. A gummy substance resulted, which was removed and boiled with 300 ml. water. The hot mixture was filtered and the filtrate was cooled. A yellow crystalline precipitate formed and was filtered off. The filtrate was reboiled with the residue to obtain a second crop of crystalline product. The combined yield was 4.17 gm. (45.0%). One crystallization from 220 ml. of 10% acetic and one crystallization from 300 ml. of 1.2 *N* hydrochloric acid gave product (XVIII), which melted with decomposition at 144°. Equiv. wt. Calc. for $C_6H_8O_4N_4S$: 232.2. Found: 231.2. Anal. Calc. for $C_6H_8O_4N_4S$: C, 31.03; H, 3.47%. Found: C, 31.15; H, 3.52%.

5-Methyl-2-nitraminothiazole (*XIV*)

To a stirred solution consisting of 4.56 gm. (0.04 mole) of 2-amino-5-methylthiazole (XIII) in 8 ml. of concentrated sulphuric acid cooled below −15°, was added a solution of 1.98 ml. (3.00 gm., 0.0475 mole) nitric acid in 2 ml. sulphuric acid during 10 min. The resulting solution was stirred and maintained below −10°, while 2 ml. of absolute alcohol was cautiously added to destroy unreacted nitric acid. The solution was quickly rinsed onto 30 gm. of chipped ice. The yellow precipitate that formed was filtered off, rinsed free of acids with water, and vacuum dried. The yield of the product melting at 195–196° with decomposition was 1.39 gm. (21.8%). One crystallization from 5% acetic acid improved the melting point to 198–199° with decomposition. The compound (XIV) could be induced to explode at 202° when heated rapidly. Anal. Calc. for $C_4H_5O_2N_3S$: C, 30.18; H, 3.14%. Found: C, 30.35; H, 3.24%.

4,5-Dimethyl-2-nitraminothiazole (*XVI*)

A solution of 2.56 gm. (0.02 mole) of 2-amino-4,5-dimethylthiazole (XV) in 4 ml. of sulphuric acid was cooled below −5°. Nitric acid (0.92 ml., 1.39 gm., 0.032 mole) dissolved in 1 ml. of sulphuric acid was added dropwise to the above solution with stirring during 10 min. About 0.5 ml. of absolute alcohol was then added cautiously to destroy unreacted nitric acid and the reaction mixture was rinsed onto 10 gm. of chipped ice. The precipitate that formed after a few minutes was rinsed with water and crystallized from 15% acetic acid. On cooling, a small granular precipitate of nitramine formed. The compound (XIV) exploded on heating at 192°. Anal. Calc. for $C_5H_7O_2N_3S$: C, 34.69; H, 4.08%. Found: C, 34.85; H, 4.08%.

Study of the Mechanism of Nitration of 2-Aminothiazole

To a mixture of 10.0 gm. (0.10 mole) of 2-aminothiazole and 15 ml. of sulphuric acid was added 4.35 ml. (6.16 gm., 0.105 mole) of nitric acid in 5 ml. of

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sulphuric acid during 10 min. with stirring and cooling to keep the temperature at −5°. After seven minutes, 10 ml. of the solution was pipetted into 10 gm. of chipped ice. The precipitated nitramine was filtered off and crystallized from 70 ml. of 95% alcohol. The purified product weighed 1.57 gm. A saturated solution of 2-nitraminothiazole was found to contain 0.55 gm. of nitramine per 100 ml. of solution. The product must then have contained 0.55 gm. × 0.70 = 0.38 gm. more nitramine before crystallization. Corrected yield 1.57 gm. +0.38 gm. = 1.95 gm. The aliquot was about 0.36 of the total reaction mixture, so when the aliquot was withdrawn there must have been 1.95 gm. ÷ 0.36 = 5.42 gm. of nitramine present, i.e. 37.4% of the thiazole present. Neutralization of the sulphuric acid filtrate gave crude 2-amino-5-nitrothiazole which after one crystallization from alcohol weighed 0.16 gm. dry (3.1%). Similarly, a second aliquot removed 67 min. after the nitric acid was added gave 1.72 gm. (33.0%) of nitramine and 0.16 gm. (3.1%) of 2-amino-5-nitrothiazole. The residual reaction mixture, 0.28 (1 − 0.36 × 2 = 0.28) of the whole, was then warmed gently on the steam bath. The temperature rose suddenly to 140° and the mixture became quite dark. It was warmed an additional 30 min. and then quenched by pouring onto 10 gm. of chipped ice. No nitramine precipitated. On neutralization with ammonia, a precipitate of 2-amino-5-nitrothiazole formed that weighed 2.14 gm. (52.7%) after one crystallization from alcohol. Corrections for solubility were not made to the weights of 2-amino-5-nitrothiazole.

Rearrangement of 2-Nitraminothiazole

To 4.7 ml. of concentrated sulphuric acid, cooled to 0°, was added 2.76 gm. (0.019 mole) of 2-nitraminothiazole, in portions. Local heating could not be avoided as the nitramine came in contact with the acid. After 10 min., the solution was poured onto 8 gm. of ice. A small precipitate (0.10 gm. dry) formed. It was filtered off and the filtrate was made alkaline with concentrated ammonia. The precipitate of 2-amino-5-nitrothiazole weighed 1.37 gm. dry (49.5%) and was pure after one crystallization from 30 ml. 10% acetic acid.

Rearrangement of 2-Nitraminothiazole in the Presence of Mesitylene

Mesitylene (3.31 gm., 0.276 mole) was suspended in 10 ml. of concentrated sulphuric acid by agitation and the mixture was kept near −5°. During 20 min., 2.0 gm. (0.138 mole) of 2-nitraminothiazole (II) was added in small portions. The mixture was then surrounded with an ice-water bath and stirred for 10 hr. The reaction mixture was then diluted to 100 ml. with water and steam distilled until 300 ml. of distillate containing a yellow solid had collected. The distillate was extracted with three 50-ml. portions of ether and the extract was dried (over anhydrous magnesium sulphate) and evaporated. An oily crystalline solid remained. The crystals were filtered from the oil and weighed 0.20 gm. Sublimation at 100° and 1 mm. pressure gave 0.10 gm. of a pale yellow solid melting at 77–83°. Crystallized from 95% alcohol the product melted at 85.0–85.5°. Reported for 2,4-dinitro-1,3,5-trimethylbenzene: m.p. 84°. The oil that was obtained was warmed on the steam bath for several hours with excess of powdered tin and hydrochloric acid. The solution was filtered

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from the tin, made alkaline with excess of sodium hydroxide, and filtered from the white precipitate. The precipitate and filtrate were separately extracted with ether and the combined extracts were evaporated nearly dry. The residue was treated with acetic anhydride. Immediately, a precipitate of fine needles formed; m.p. 330–334° decomp. Sublimation at 190° and 0.2 mm. pressure did not improve the melting point. One crystallization from absolute alcohol raised the melting point to 344–346° with decomposition. Reported for 1,3-diacetamido-1,3,5-trimethylbenzene: m.p. 320–325°. Anal. Calc. for $C_{13}H_{18}O_2N_2$: C, 66.64; H, 7.74%. Found: C, 66.48; H, 7.87%.

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THE REACTIONS OF ACTIVE NITROGEN WITH ORGANIC MOLECULES[1]

By H. G. V. Evans,[2] G. R. Freeman,[2] and C. A. Winkler

ABSTRACT

The main features of the reactions of active nitrogen with various organic molecules are reviewed, and a unified mechanism outlined to account for at least the more significant experimental observations.

INTRODUCTION

Lewis (23) discovered active nitrogen in 1900. He observed that when nitrogen at low pressure was subjected to a condensed discharge, a yellow mist filled the discharge tube and diffused into the connecting tubes. On breaking the current, a yellow afterglow persisted for several seconds. He showed that the afterglow gave a banded spectrum which could be identified with part of the N_2 spectrum.

In 1911, Strutt (later, Lord Rayleigh) began an extensive study of the physical and chemical properties of nitrogen treated by the Lewis method (12, 13, 34, 40 to 47). He found it to be very reactive chemically. Vapors of many metallic and non-metallic elements (e.g. cadmium, sodium, arsenic, sulphur) were converted to nitrides. Carbon disulphide, sulphur chloride, and hydrogen sulphide yielded a polymeric nitrogen sulphide. Hydrocarbons gave hydrogen cyanide as the main product, while halogenated hydrocarbons gave products from which cyanates were obtained by treatment with potassium hydroxide. All the reactions with organic compounds were accompanied by the brilliant emission of the CN spectrum. The hydrocarbons gave both the red and violet CN bands and the flames appeared lilac in color. When halogen atoms were present in the molecule, the red bands were more strongly developed; this was particularly marked with CCl_4, $CHCl_3$, $CHBr_3$, ethylene dichloride, and ethylidene chloride all of which gave strong orange cyanogen emission. Ethyl chloride and methyl bromide gave flames of intermediate character.

Although most of the early studies of the chemical reactivity of active nitrogen were qualitative in nature (22, 53, 54) the reactions with hydrogen (6, 22, 39) and with nitric oxide and nitrogen dioxide (37) were studied in some detail. Reasonable mechanisms involving atomic nitrogen were suggested for these reactions.

Investigations into the reactions of active nitrogen with various types of molecules, particularly the hydrocarbons and chlorinated hydrocarbons, have been in progress in this laboratory during the past ten years. It seems appropriate at this time to review the main characteristics of these reactions

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and to attempt a consistent interpretation of the reaction mechanisms. In so doing, atomic nitrogen will be assumed to be the main reactive species in active nitrogen, for reasons outlined previously (8).

THE REACTIONS OF ACTIVE NITROGEN WITH ORGANIC MOLECULES

The reactions to be discussed were studied in a conventional fast flow system. Nitrogen at a known flow rate was activated by a condensed discharge and introduced into a reaction vessel where it was mixed with the second reactant which also entered at a measured rate through a fine jet. The products were suitably trapped and analyzed by appropriate methods. Experimental details may be obtained by reference to the original papers.

Unsaturated Hydrocarbons

Ethylene

In the first study (18) the products of this reaction were identified as hydrogen cyanide and some ethane. A viscous polymer was also formed, which was probably a polymer of hydrogen cyanide. The yield of hydrogen cyanide increased linearly with ethylene flow rate until a maximum was reached, and then remained constant. Wrede gauge (55) measurements of nitrogen atom concentrations corresponded approximately to the maximum yield of hydrogen cyanide. This indicated that the reaction was fast enough to go to virtual completion in the flow time through the reaction vessel. The yield of ethane increased markedly at higher ethylene flow rates.

In a more detailed study (49) of the reaction, with improved experimental techniques, polymerization of hydrogen cyanide was avoided and material balances of about 98% obtained. It was confirmed that the reaction proceeds by complete consumption of nitrogen atoms in the presence of excess ethylene, and by complete consumption of ethylene in the presence of excess nitrogen atoms. In addition to hydrogen cyanide and ethane, smaller amounts of acetylene, cyanogen, and methane were found in the products. The amount of cyanogen formed increased rapidly with increasing ethylene flow rate when nitrogen atoms were in excess, and then decreased as the ethylene flow rate increased beyond the equivalence point. The amounts of methane and acetylene showed similar behavior, although the change in yield was less striking. At the flow rate where both ethylene and nitrogen atoms were completely consumed, the products of the reaction were hydrogen cyanide (75%), ethane (10%), methane (9%), acetylene (3%), and cyanogen (2%).

Acetylene

The products of this reaction were (50) hydrogen cyanide, a polymer that contained approximately 32% nitrogen, and smaller amounts of cyanogen, methane, and hydrogen. At very low flow rates of acetylene, corresponding to at least a sevenfold excess of nitrogen atoms, the only product was polymer. The yield of hydrogen cyanide and polymer increased to constant values with increase of acetylene flow rate. The yield of cyanogen passed through a maximum at an acetylene flow rate near the value corresponding to the complete consumption of nitrogen atoms. The individual yields of hydrogen

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and methane were erratic but the total hydrogen contained in both these products showed a regular dependence on acetylene flow rate, with a maximum yield for a flow rate slightly greater than that required for complete consumption of nitrogen atoms.

Propylene

Hydrogen cyanide and ethylene were the main products of this reaction (48), together with smaller quantities of ethane and propane, and traces of acetylene and of a C_4 fraction. The appearance of C_2 hydrocarbons as the principal product leaves little doubt that the main reaction is the removal of one carbon atom by an attacking nitrogen atom. The yields of propane and ethane paralleled the amounts of propylene and ethylene recovered, and it may be concluded that the saturated products were formed mainly by hydrogenation of the corresponding olefin.

Butenes

The reactions of nitrogen atoms with butene-1, *cis*-butene-2, and isobutene (16) all gave hydrogen cyanide as a main product, together with propylene and ethylene, and smaller quantities of butane, propane, ethane, and methane. All the reactions showed complete consumption of nitrogen atoms at high hydrocarbon flow rates. Apparently the first step in all three reactions led to the formation of hydrogen cyanide, propylene, and a hydrogen atom. The order of reactivities with nitrogen atoms was butene-1 > *cis*-butene-2 > isobutene. Increasing temperature favored the reactions of butene-1 and *cis*-butene-2, but not that of isobutene, so that the lower rate of the isobutene reaction is probably the result of a lower steric factor.

Saturated Hydrocarbons

Methane

Hydrogen cyanide is the only product that has been detected in this reaction (3, 15) in the type of system used. Hydrogen cyanide production was small at all flow rates at temperatures below about 250°C. At higher temperatures, the yield of hydrogen cyanide was low at low methane flow rates but increased rapidly as the methane flow rate was increased. This effect appeared to be due to attack on methane by hydrogen atoms, since the initial low rates of HCN formation could be markedly increased by the addition of appropriate amounts of atomic hydrogen to the system.

Ethane

The only product detected in this reaction was hydrogen cyanide (3, 15), and a good carbon balance was obtained. At temperatures above 165°C., the reaction was found to proceed by complete consumption of nitrogen atoms when ethane was in excess. Under these conditions, production of hydrogen cyanide corresponded to about 85% of the atom concentration inferred from Wrede gauge measurements. When the reaction was studied over a wide range of temperature (15), there appeared to be a distinct difference in activation energies at low and high temperatures.

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Propane

The products of this reaction were identified (31) as hydrogen cyanide, acetylene, ethylene, and ethane. Complete consumption of nitrogen atoms was not attained at 63°C., but was attained at 250°C. for a ratio of propane to nitrogen atoms greater than 1.3. Of particular significance was the recovery of ethylene and acetylene in the region of incomplete consumption of nitrogen atoms. The reaction of N atoms with these unsaturated compounds is at least 10 times more rapid than the reaction with propane, so that the recovered ethylene and acetylene can represent only a small fraction of the amounts formed.

Butanes

Hydrogen cyanide and smaller amounts of ethylene and acetylene were obtained from both *n*-butane and isobutane (2). The predominance of unsaturated hydrocarbons in the secondary products was similar to that found for propane, and the amounts formed in the course of reaction must have been much greater than the amounts recovered.

Neopentane

Large quantities of hydrogen cyanide and small quantities of ethylene, acetylene, propylene, and propane were obtained from this reaction (32). Complete consumption of active nitrogen was attained only at 250°C. for a ratio of neopentane to nitrogen atom flow rates greater than 1.3. As with ethane, there appeared to be two activation energies associated with the reaction when it was studied over a wide range of temperature.

Cycloparaffins

The reactions of active nitrogen with cyclopropane and with cyclobutane (25, 30) are similar to the reactions with propane and the butanes. Cyclopropane is somewhat less reactive than propane, while cyclobutane and the open chain butanes have comparable reactivities.

Kinetic Data for the Hydrocarbon Reactions

It has not been possible to obtain any values of the activation energies and steric factors for the reactions of active nitrogen with the olefins and acetylene, owing to their relatively high rates. An early attempt (19) to apply diffusion flame technique to the ethylene reaction indicated that the activation energy was probably less than 3 kcal. and the steric factor possibly of the order 10^{-2}.

Orders of magnitude for the activation energies and steric factors of the reactions with saturated hydrocarbons have been estimated from rough values of the second order rate constants calculated for hydrogen cyanide production at different temperatures. The calculations have generally been made assuming both streamlined and turbulent gas flow through the reaction vessel. The activation energies and steric factors that have been obtained are given in Table I.

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TABLE I

Hydrocarbon	E (kcal.)		P		Ref.
	Streamlined flow	Turbulent flow	Streamlined flow	Turbulent flow	
Methane*	11 to 13		10^{-2} to 10^{-3}		(3, 15)
Ethane	6.2	7.9	3×10^{-3}	7×10^{-2}	(3)
High temp. range	5.7	6.3	6.4×10^{-4}	2.0×10^{-3}	(15)
Low temp. range	2.7	2.4	1.4×10^{-5}	1.2×10^{-5}	
Propane	5.1	6.2	9.1×10^{-4}	2.1×10^{-2}	(31)
n-Butane	3.6		4.5×10^{-4}		(2)
Isobutane	3.1		4.4×10^{-4}		(2)
Neopentane					
High temp. range	6.5	7.7	2.7×10^{-4}	4.9×10^{-2}	(32)
Low temp. range	2.0	2.0	1.1×10^{-6}	3.3×10^{-5}	
Cyclopropane	3.2	4.0	1.9×10^{-5}	5×10^{-4}	(25, 30)
Cyclobutane	4.6	6.4	1.5×10^{-4}	4.1×10^{-2}	(30)

**Values for this reaction might have little or no significance owing to demonstrated complications by hydrogen atom reactions. For the same reason, no attempt is made to discuss this reaction in the present paper.*

Alkyl Chlorides

In their rates, these reactions appeared to resemble the analogous reactions with unsaturated hydrocarbons (7). The reactions of all the halides yielded hydrogen cyanide and hydrogen chloride as main products, and small amounts of cyanogen and a polymer that contained carbon, hydrogen, nitrogen, and chlorine. No cyanogen chloride, chlorine, or methane was obtained from any of the reactions. The halides, other than methyl chloride, yielded small amounts of C_2 hydrocarbons (mainly ethylene and acetylene) while the propyl chlorides also gave small yields of C_3 hydrocarbons (mainly propylene). At higher flow rates of the organic chlorides, the yields of products approached limiting values. With methyl chloride, an increase in limiting yield with increase of temperature was observed. It was also observed with methyl chloride that some unchanged reactant was recovered at lower flow rates, in spite of a linear relation between product formation and methyl chloride flow rate.

Methyl Cyanide

The main product of this reaction, over a wide temperature range, was hydrogen cyanide (11). Smaller amounts of cyanogen, methane, ethane, ethylene, acetylene, and (probably) methyl isonitrile were also recovered. The yields of primary products, in relation to the methyl cyanide flow rate, indicated complete consumption of active nitrogen at each temperature, but the maximum yield increased markedly with increase of temperature (cf. methyl chloride).

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Methylamine

This reaction yielded hydrogen cyanide and smaller amounts of ammonia and a polymer, together with traces of cyanogen, methane, ethane, ethylene, and acetylene (14). The rates of methylamine destruction and hydrogen cyanide formation increased, and polymer formation decreased, with increase of temperature.

REACTION MECHANISMS

On the basis that atomic nitrogen is responsible for the reactions of active nitrogen with organic molecules (8), it is possible to calculate the energetics of individual reaction steps and, with due regard for the uncertainty in many of the energy values used, to suggest energetically reasonable mechanisms to explain the experimental results.

The products of the atomic nitrogen reactions with saturated hydrocarbons of more than two carbon atoms are generally similar to those of the reactions with the corresponding olefins. This similarity is strongly emphasized by the behavior of the alkyl halides in their resemblance to the olefins when attacked by nitrogen atoms (7). It seems reasonable, therefore, to suggest similar mechanisms for molecules with the same number of carbon atoms. It is convenient to discuss first the probable mechanisms for reactions of the olefins, as a basis for a unified mechanism for the other reactions.

Olefins

Ethylene

The only reaction with ethylene that is energetically favorable is

$$N + C_2H_4 \rightarrow HCN + CH_3 + 62\ \text{kcal.}^3 \qquad [1]$$

This reaction involves both a change in spin (8) and the movement of a hydrogen atom from one carbon atom to the other. There is every reason to expect that a nitrogen atom and an ethylene molecule will form a relatively long-lived complex even before the change in spin occurs.[4] The emission of the reaction flame and the formation of cyanogen and acetylene provide direct evidence that such complexes are formed (see below). Thus, it seems quite possible that the complex will have sufficiently long lifetime to permit both the change in spin and the movement of the hydrogen atom (which might take place after the change in spin).

The observed products from ethylene, together with the results obtained in a study of the reaction of azomethane with nitrogen atoms (1), indicate that methyl radicals formed in reaction [1] react very rapidly with nitrogen atoms,

$$N + CH_3 \rightarrow HCN + 2H + 10\ \text{kcal.} \qquad [2]$$

Reaction [2] is spin-allowed for three-eighths of the collisions (8) and should not have a significant energy barrier. Most of the hydrogen atoms formed by

[3] *Values for the heats of reaction have been calculated from heats of formation given in the Appendix.*

[4] *The repulsion due to exchange forces during the initial approach of the nitrogen atom should be small since p-electrons are involved, and delocalized orbitals embracing the π-orbitals of the carbon–carbon bond and the nitrogen atomic orbitals should lead to considerable lowering of the potential energy, particularly after the change in spin has occurred (8).*

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reaction [2] must ultimately have recombined to form H_2, although this was not determined directly. However, the manner in which ethane production varied with ethylene flow rate (49) at the higher flow rates where olefin was in excess shows that most of the ethane in this region was probably formed by the well-known reactions

$$H + C_2H_4 \rightarrow C_2H_5, \quad [3]$$

$$C_2H_5 + H_2 \rightarrow C_2H_6 + H. \quad [4]$$

Hence, reaction [2] must form predominantly two hydrogen atoms rather than molecular hydrogen.

The sharp maximum in the cyanogen production from ethylene makes it seem very likely that cyanogen was formed by reaction between a nitrogen atom and a nitrogen atom – ethylene complex. It is possible that some cyanogen might be formed directly,

$$N + N.C_2H_4 \rightarrow 2(CN)_2 + 2H_2 + (91-q) \text{ kcal.}, \quad [5]$$

where q is the heat evolved in forming the complex,

$$N + C_2H_4 \rightarrow N.C_2H_4 + q.$$

However, this reaction involves a great deal of rearrangement, and it appears more likely that cyanogen was formed by recombination of cyanogen radicals. The reaction

$$N + N.C_2H_4 \rightarrow N_2 + C_2H_4 + (226-q) \text{ kcal.} \quad [6]$$

is very exothermic, and there should be a good chance that the C_2H_4 part of the complex receives enough energy to dissociate into very reactive fragments that then react with a nitrogen atom to form CN radicals, e.g.

$$N + N.C_2H_4 \rightarrow N_2 + 2CH_2^* + (68-q) \text{ kcal.}, \quad [7]$$

$$CH_2^* + N \rightarrow CN + H_2 + 104 \text{ kcal.}, \quad [8]$$

$$2CN \rightarrow (CN)_2, \quad [9]$$

where CH_2^* represents a methylene radical in the triplet state.

Cyanogen radicals may also be formed to some extent from simple reactions, e.g.

$$N + CH_3 \rightarrow CN + H + H_2 - 1 \text{ kcal.} \quad [10]$$

However, the predominance of HCN over $(CN)_2$ observed in the products indicates that reaction [10] occurs far less than reaction [2], and the manner in which cyanogen production varies with ethylene flow rate indicates that reactions resulting from recombination of nitrogen atoms are the more important source of CN radicals.

Reaction [8] is sufficiently exothermic to give the electronically excited CN radicals that emit the reaction flame, and the chemiluminescent reaction of nitrogen atoms with methylene radicals (or with CH radicals which can also be formed in exothermic reactions similar to reaction [7]) may well contribute to the reaction flame.

Two of the products, cyanogen (40) and hydrogen cyanide (5), give cyanogen flames with active nitrogen, probably by such reactions as

$$N + N.C_2N_2 \rightarrow N_2 + CN + CN^* + (112-E) \text{ kcal.}, \quad [11]$$

$$N + N.HCN \rightarrow N_2 + CN^* + H + (111-E) \text{ kcal.}, \quad [12]$$

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where E is the electronic excitation energy of CN* above the ground state. However, for organic molecules the flame color varies with the reactant, and there seems to be little doubt that there is more than one mechanism of flame emission.[5]

The reactions

$$N + N.C_2H_4 \rightarrow N_2 + C_2H_4^*, \quad [13]$$

$$C_2H_4^* \rightarrow C_2H_2^* + H_2, \quad [14]$$

$$C_2H_2^* \rightarrow C_2H_2, \quad [15]$$

where $C_2H_4^*$ and $C_2H_2^*$ and represent ethylene and acetylene in triplet states, should occur with quite high probability (8), and may well account for the formation of acetylene in the ethylene reaction. The fact that acetylene production decreases more slowly than cyanogen production at the higher ethylene flow rates gives some indication that vibrationally excited molecules may also give some acetylene by the reaction

$$N_2\dagger + C_2H_4 \rightarrow N_2 + C_2H_4^* \quad [16]$$

followed by reactions [14] and [15]. The close analogy between reactions [13] and [16] will be obvious.

These considerations indicate that acetylene and cyanogen are mainly formed as by-products of the recombination of nitrogen atoms. Further evidence for a catalyzed recombination of nitrogen atoms is to be found in the recovery of significant amounts of methane and ethane in the region where ethylene is completely consumed. If the concentration of nitrogen atoms were not reduced markedly in this region by catalyzed recombination, and remained as high as indicated by the maximum hydrogen cyanide recovery, it is difficult to see how reactions which are probably responsible for the formation of methane and ethane in this region, viz.

$$CH_3 + H_2 \rightarrow CH_4 + H, \quad [17]$$

$$CH_3 + H \rightarrow CH_4, \quad [18]$$

$$CH_3 + CH_3 \rightarrow C_2H_6, \quad [19]$$

could compete successfully with the very fast reaction

$$CH_3 + N \rightarrow HCN + 2H. \quad [2]$$

Propylene

The observed production of ethylene in this reaction leaves little doubt that it is a primary product. At first sight, the spin-disallowed reaction

$$N + C_3H_6 \rightarrow HCN + H + C_2H_4 + 27 \text{ kcal.} \quad [20]$$

seems to be the most likely. However, unless there is a great deal of rearrangement remote from the point of attack, nitrogen atom attack at the double bond should lead to ethylidene radicals rather than ethylene. On the other hand, the reaction similar to the main ethylene reaction

$$N + C_3H_6 \rightarrow HCN + C_2H_5 + 65 \text{ kcal.} \quad [21]$$

[5] *Flame emission may also be due in part to resonance transfer from* vibrationally *excited, ground state molecules of nitrogen in active nitrogen (8),*

$$CN + N_2\dagger \rightarrow CN^* + N_2.$$

Since $N_2\dagger$ molecules also lose vibrational energy by collision, predominantly by one-quantum transfers (8), their energy content and hence the energy received by CN radicals may well depend markedly on the presence of foreign molecules.*

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might form ethyl radicals with enough energy to permit the reaction

$$C_2H_5 \rightarrow C_2H_4 + H - 38 \text{ kcal.} \quad [22]$$

Reaction [22] has an activation energy of about 40 kcal. (38), so that it would be expected to occur if less than about 20 kcal. involved in reaction [21] resided as translational energy and vibrational excitation of the hydrogen cyanide. Since it certainly requires more than 7 kcal. to form the ethylidene radical from ethylene, it seems likely that the reactions of ethylene and propylene with nitrogen atoms are similar, with the difference that the ethyl radical from propylene decomposes either during or immediately after the primary reaction.

Ethylene formed by reaction [22] would react with nitrogen atoms as outlined previously.

The manner in which production of propane and ethane varied with propylene flow rate immediately suggests that the saturated products were formed by reactions of hydrogen atoms with the corresponding olefins.

Butenes

The reactions of the butenes are very similar to the reaction of propylene and comment is required only for the reaction

$$N + CH_3—CH=CH—CH_3 \rightarrow C_3H_6 + HCN + H. \quad [23]$$

Since movement of a hydrogen atom from one carbon atom to another apparently occurs in the ethylene reaction, and probably also in the propylene reaction, it may seem strange that, for reaction [23], a methyl group should move instead. However, if, as seems likely, the favored line of approach of the nitrogen atom to the double bond is between the two hydrogen atoms of *cis*-butene-2, the closer approach of the nitrogen atom to one of the carbon atoms may prevent the hydrogen atom on this carbon from shifting and the shift of the methyl group should be highly favored energetically. Hence, the reaction probably occurs by

$$N + CH_3—CH=CH—CH_3 \rightarrow CH_3—CH—CH_3 + HCN \quad [24]$$

followed immediately by

$$CH_3—CH—CH_3 \rightarrow CH_3CH=CH_2 + H. \quad [25]$$

Unified Mechanism

On the basis of the previous discussion it is possible to suggest a fairly consistent mechanism for other reactions of active nitrogen with organic molecules that have been studied. The main features can be illustrated by comparison of the suggested mechanisms for propylene, the propyl chlorides, and propane. The observed products of these reactions can be explained if it is assumed that a chemically identical complex is formed in all the reactions:

$$N + C_3H_6 \rightarrow N.C_3H_6, \quad [26]$$

$$N + C_3H_7Cl \rightarrow N.C_3H_6 + HCl, \quad [27]$$

$$N + C_3H_8 \rightarrow N.C_3H_6 + H_2. \quad [28]$$

The differences observed are then ascribed to the increased stability of the complex in going from propylene to propane (the energy content of the com-

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plex obviously decreases in that order), and to differences in ease of formation of the complexes. The formation of unsaturated hydrocarbons as secondary products can then be explained by calling on conservation of spin and the reluctance of molecular systems to transfer large amounts of internal energy into translational energy. Thus, a reaction scheme that can account for the unsaturated products from the propane and propyl chloride reactions is:

$$N + N.C_3H_6 \rightarrow C_3H_6^* + N_2 + (226 - E_1 - q) \text{ kcal.} \quad [29]$$

followed by[6]

$$C_3H_6^* \rightarrow C_2H_4^* + CH_2 + (E_1 - E_2 - 70) \text{ kcal.}, \quad [30]$$

or

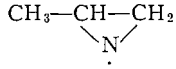
$$C_3H_6^* \rightarrow C_2H_4 + CH_2^* + (E_1 - E_3 - 70) \text{ kcal.}, \quad [31]$$

and

$$C_2H_4^* \rightarrow C_2H_2^* + H_2 + (E_2 - E_4 - 42) \text{ kcal.}, \quad [32]$$

where q is the heat evolved in forming the $N.C_3H_6$ complex from N and C_3H_6 (derived from each reactant) and E_1, E_2, E_3, and E_4 are the excitation energies to reach the triplet states $C_3H_6^*$, $C_2H_4^*$, CH_2^*, and $C_2H_2^*$ respectively. If $C_2H_4^*$ is ethylene in a triplet state, the value of E_2 must be more than 90 kcal. (8) for reaction [32] to occur and it might be expected that the ratio of acetylene to ethylene formed would be much lower than that observed.

However, if, as seems reasonable, the structure of $N.C_3H_6$ is essentially



the most likely structure for $C_2H_4^*$ formed by reaction [30] should be $(CH_3—CH:)^*$, the ultimate fate of which will be determined by the relative probabilities of the spin-disallowed reactions

$$(CH_3—CH:)^* \rightarrow C_2H_4, \quad [33]$$

$$\rightarrow C_2H_2 + H_2. \quad [34]$$

It seems quite reasonable, then, that nearly equal amounts of acetylene and ethylene might be formed.

The value of E_1, hence the probability of reaction [30], should be quite sensitive to the extent of interaction between the nitrogen atom and the rest of the $N.C_3H_6$ complex. It might be expected to increase with increasing stability of the $N.C_3H_6$ complex, i.e. to increase from propylene to propyl chloride to propane. The amount of propylene formed by reaction [29] followed by

$$C_3H_6^* \rightarrow C_3H_6 \quad [35]$$

should therefore be greatest for propylene and least for propane.

In all the reactions, spontaneous decomposition of the complexes will also occur

$$N.C_3H_6 \rightarrow HCN + C_2H_5 \quad [36]$$

[6]*Spin-allowed reactions of the type*

$$C_3H_6^* \rightarrow C_2H_3 + CH_3,$$

$$C_3H_6^* \rightarrow C_3H_5 + H$$

might well occur, but these presumably would also lead to formation of unsaturated products.

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followed by

$$N + C_2H_5 \rightarrow HCN + H + CH_3, \quad [37]$$

$$N + CH_3 \rightarrow HCN + 2H. \quad [2]$$

The C_2H_5 radicals formed in the propylene reaction should receive much more energy than those formed in the propyl chloride or propane reactions because of the relative energy contents of the complexes. Thus, it seems likely that the subsequent reaction

$$C_2H_5 \rightarrow C_2H_4 + H \quad [22]$$

might occur to a significant extent only in the propylene reaction, where it is probably responsible for most of the ethylene formed.

Both the formation of $N.C_3H_6$ complexes and their spontaneous decomposition should be slowest for propane, and somewhat, though probably not much faster for propylene than for the propyl chlorides. These considerations account for the formation of a much larger ratio of acetylene to ethylene in the C_2 products from propane and the propyl chlorides than from propylene, and for the formation of nearly as much propylene as ethylene in the propyl chloride reactions.

The reactions of the butanes and the cycloparaffins with active nitrogen may be treated in a manner entirely analogous to that outlined above, and discussion of them would seem to be superfluous.

The reactions for ethyl chloride corresponding to those for the C_3 molecules would be

$$N + N.C_2H_4 \rightarrow N_2 + C_2H_4^*, \quad [38]$$

$$C_2H_4^* \rightarrow C_2H_4, \quad [39]$$

$$C_2H_4^* \rightarrow C_2H_2 + H_2. \quad [40]$$

It seems reasonable that, for this reaction, $C_2H_4^*$ should be $(\dot{C}H_2-\dot{C}H_2)^*$, so that the spin-allowed reaction to form ethylene should be favored. Hence, much less acetylene than ethylene should be expected from the ethyl chloride reaction, and this is indeed observed. The small amount of acetylene formed might have resulted from the spin-allowed reaction

$$C_2H_4^* \rightarrow C_2H_2^* + H_2 \quad [41]$$

followed by

$$C_2H_2^* \rightarrow C_2H_2. \quad [42]$$

The reaction of ethane with active nitrogen yielded no ethylene or acetylene. It would appear, therefore, that a stable $N.C_2H_4$ complex (analogous to $N.C_3H_6$ from propane) is not formed. Nevertheless, the only reasonable mechanism for the direct reaction of ethane with nitrogen atoms is completely analogous to the corresponding ethylene and ethyl chloride reactions, viz.

$$N + C_2H_6 \rightarrow HCN + CH_3 + H_2 + 30 \text{ kcal.}, \quad [43]$$

$$N + CH_3 \rightarrow HCN + 2H. \quad [2]$$

The inference that the reaction

$$N + C_2H_6 \rightarrow N.C_2H_4 + H_2 + (q-33) \text{ kcal.} \quad [44]$$

does not occur seems reasonable. This reaction would be highly endothermic unless q, the binding energy of $N.C_2H_4$, is large, which must require a change

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of spin. Ethane has fewer degrees of freedom than propane, and the lifetime of a collision complex with a nitrogen atom, and hence the chance for a change of spin during the collision, will be correspondingly reduced.[7] Thus, reaction [43] probably occurs as a straightforward spin-disallowed reaction. Unfortunately, the reaction with ethane appears to be complicated, since different activation energies were obtained in the low and high temperature ranges. It is possible (8) that there is a contribution from the indirect reaction

$$N_2\dagger + C_2H_6 \rightarrow N_2 + C_2H_5 + H \qquad [45]$$

followed by

$$N + C_2H_5 \rightarrow HCN + H + CH_3. \qquad [37]$$

With alkyl halides, which react rapidly with atomic nitrogen, the reaction analogous to [45] should be, for example,

$$C_2H_5Cl + N_2\dagger \rightarrow C_2H_5 + Cl + N_2. \qquad [46]$$

Since there was no evidence for the formation of significant amounts of atomic chlorine in any of the alkyl halide reactions, it seems safe to conclude that reactions of the type of reaction [45] are unable to compete with fast nitrogen atom reactions.

Since the reaction of active nitrogen with ethane showed a change of activation energy with temperature, there is a possibility that it is carried by hydrogen atoms in the manner demonstrated for the analogous reaction with methane, i.e.

$$H + C_2H_6 \rightarrow H_2 + C_2H_5 \qquad [47]$$

followed by nitrogen atom reactions with the alkyl radicals.

Acetylene and vinyl chloride behave similarly in their reactions with atomic nitrogen, and a chemically identical intermediate is probably formed in both reactions,

$$N + C_2H_2 \rightarrow N.C_2H_2, \qquad [48]$$

$$N + C_2H_3Cl \rightarrow N.C_2H_2 + HCl. \qquad [49]$$

Direct evidence for significant concentrations of $N.C_2H_2$ in the acetylene reaction is provided by the recovery of a polymer with a composition close to that expected for $(N.C_2H_2)_n$.

The heats of formation of CN, CH_2, etc., are not well enough established to permit any conclusions about the detailed mechanisms of these two reactions. The long lifetime of the $N.C_2H_2$ complex indicates that the spin-allowed reaction

$$N + C_2H_2 \rightarrow CN + CH_2^* - 12 \text{ kcal.} \qquad [50]$$

probably has a significant activation energy. On the other hand, similar production of HCN from acetylene and vinyl chloride by the spin-disallowed reaction

$$N.C_2H_2 \rightarrow HCN + CH - (q+6) \text{ kcal.} \qquad [51]$$

would seem improbable, since it would require that the heat of sublimation of

[7] *It is significant that ethyl chloride appears to be able to form the $N.C_2H_4$ complex. Owing to the presence of the heavy chlorine atom, the vibrational levels will be more closely spaced in ethyl chloride than in ethane and the chance of redistributing the collision energy among the internal degrees of freedom, and hence the collision lifetime, should be greater.*

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graphite should be considerably less than the generally accepted value (170 kcal.), so that such a reaction would be exothermic even for $N.C_2H_2$ derived from vinyl chloride.

It is possible that most of the hydrogen cyanide production results from reactions of the type

$$N + N.C_2H_2 \rightarrow 2HCN + (218-q) \text{ kcal.}, \quad [52]$$

$$\rightarrow HCN + H + CN + (103-q) \text{ kcal.} \quad [53]$$

The reactions of methyl chloride, methyl cyanide, and methylamine, unlike the reaction of methane itself, appear to involve formation of relatively long-lived complexes. The observed increase in limiting yield of hydrogen cyanide with increase of temperature (7, 11, 14) can be explained if nitrogen atoms are destroyed by recombination catalyzed by the reactant; a quantitative treatment of the data for methyl cyanide on this basis gives good agreement with experiment (10). Recombination catalyzed by reactant should occur most readily if a complex is formed and should lead to side reactions. Thus, the reaction[8]

$$N + N.CH_3X \rightarrow N_2 + CH_3X \quad [54]$$

is exothermic by more than 200 kcal., and there should be a good chance that the CH_3X part of the complex should receive enough energy in internal degrees of freedom to dissociate into reactive fragments that can react very fast with atomic nitrogen, or among themselves to form the products such as cyanogen, acetylene, ethylene observed in the methyl chloride, methyl cyanide, and methylamine reactions.

The observed products of the methyl chloride reaction (7) clearly indicate that the primary reaction is

$$N + CH_3Cl \rightarrow HCN + HCl + H. \quad [55]$$

It seems likely that the main reaction responsible for hydrogen cyanide production in the methyl cyanide reaction [11] is similar, i.e.

$$N + CH_3CN \rightarrow 2HCN + H. \quad [56]$$

Thus, these two reactions probably resemble the ethylene reaction

$$N + C_2H_4 \rightarrow HCN + CH_3. \quad [1]$$

The analogous reaction with methylamine would be

$$N + CH_3NH_2 \rightarrow HCN + H + NH_3. \quad [57]$$

While the relation between ammonia production and methylamine flow rate (14) might be interpreted to indicate that ammonia is a primary product of the reaction, the amount of ammonia produced is only about one quarter the amount of hydrogen cyanide formed in the temperature range 84° to

[8]*By analogy with the unified mechanism, it may be expected that the intermediate complex would be formed by elimination of HX, e.g.*

$$N + CH_3Cl \rightarrow N.CH_2 + HCl.$$

This would still lead to catalyzed recombination and would, if anything, make it easier to understand the formation of C_2H_2 and C_2H_4 in the methyl cyanide and methylamine reactions. However, recovery of some methyl chloride even at the lowest flow rates used (7) indicates that elimination of HX is not essential for relatively stable complexes to be formed.

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477°C. Hence, ammonia is probably not a primary product, and the primary reaction might well be analogous to that of ethane with nitrogen atoms, i.e.

$$N + CH_3NH_2 \rightarrow HCN + H_2 + NH_2 \quad [58]$$
$$(\text{cf. } N + C_2H_6 \rightarrow HCN + H_2 + CH_3).$$

This would suggest that the hydrogens of the NH_2 group, like those of the CH_3 group in ethane, make it difficult for transfer of an additional hydrogen to these groups.

Like methylamine, neopentane appears to resemble ethane in its reaction with atomic nitrogen. A primary reaction analogous to that suggested by the unified mechanism for saturated hydrocarbons of more than two carbon atoms would require the shift of a methyl group

$$C(CH_3)_4 + N \rightarrow (CH_3)_2C.CH.CH_3.N + H_2 \quad [59]$$

or elimination of methane instead of hydrogen,

$$C(CH_3)_4 + N \rightarrow (CH_3)_2C.CH_2.N + CH_4. \quad [60]$$

Neither process seems probable, and it is likely that the nitrogen atom attacks at a carbon–carbon linkage, as in ethane,

$$\begin{array}{l} CH_3 \\ | \\ CH_3—C—CH_3 \\ | \\ CH_3 \end{array} + N \rightarrow \begin{array}{l} CH_3 \\ \\ CH_3—C—CH_3 \\ | \\ CH_3 \end{array} + HCN + H_2 \quad [61]$$

followed by fast reaction of the C_4H_9 radicals to give more HCN and the unsaturated products observed.

The observed change in apparent activation energy with temperature might reflect a contribution from a reaction of the type

$$C(CH_3)_4 + N_2\dagger \rightarrow N_2 + C(CH_3)_3 + CH_3 \quad [62]$$

or perhaps the intervention of hydrogen atom attack, as with methane.

GENERAL DISCUSSION

One of the most interesting implications of the mechanisms suggested above is the ease of approach of the nitrogen atom to a completely shielded carbon atom, as in the alkyl chloride reactions. The theoretical approximation known as the "perfect pairing" approximation (9) should apply to the initial approach of a nitrogen atom. According to this approximation the interaction between the electrons in the outer orbitals of the nitrogen atom and those in the paired orbitals of the other reactant would give the usual coulomb and exchange terms, the former leading to attraction and the latter to repulsion. For *s*-electrons the exchange terms predominate, but for *p*-electrons the attractive coulomb terms are more important. Since the outer valence electrons of nitrogen, carbon, and chlorine are all *p*-electrons, it seems likely that the original approach of a nitrogen atom to an alkyl halide molecule will not be accompanied by a large increase in potential energy. Experimental confirmation of this is given by a recent study (33) of chlorine atom reactions in which, on the basis that the ease of approach depends on the electron affinities of the approaching particles, the relative activation energies for the

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reactions of methane with Cl, H, and CH_3 are explained. This implies that the attractive forces result mainly from ionic structures in which electrons have shifted from the carbon bonds to the approaching radical.

When the nitrogen atom comes closer to the carbon atom, the approximation of perfect pairing would be expected to break down, and a better approximation would probably be given by delocalized molecular orbitals embracing nitrogen and carbon atomic orbitals, and either a hydrogen or a chlorine atomic orbital. Such a delocalization would result in the removal of at least part of the directional character of the carbon–hydrogen and carbon–chlorine bonds, and the decrease in potential energy accompanying the closer approach of the nitrogen atom to the carbon atom would be expected to offset most of the energy required to move the other atoms out of the way. From the valence bond point of view, this delocalization would be described as a contribution from several ionic structures involving, for example, a positive charge on a hydrogen atom and a negative charge on the nitrogen atom (corresponding to partial transfer of electrons from the C—H orbitals to the C—N orbitals). The tendency for a hydrogen atom to receive a positive charge would result in an attractive force between it and the polarizable chlorine atom, and it seems quite likely that one of the hydrogens and the chlorine atom would approach to form hydrogen chloride as both atoms were forced out of the way of the approaching nitrogen atom. Moreover, the loss of directional character, and perhaps also the tendency to form protons, should make it relatively easy for hydrogen shifts to occur as required by the unified mechanism presented previously. The directional character of carbon–hydrogen bonds is the basis for the conclusion of Rice and Teller (35) that direct attack at a completely shielded carbon atom requires a high activation energy. From the considerations given above, it appears likely that the directional character of such bonds will be lost on the close approach of a sufficiently electronegative radical.

If it is granted that there should be no large energy barrier in the reaction of nitrogen atoms with alkyl halides, it is interesting to consider whether a high rate of reaction implies little restriction to a change of spin. The main decrease in potential energy corresponding to delocalized orbitals will probably occur only after a pairing of spins (8), since the Pauli exclusion principle will allow lower orbitals to be occupied when more of the spins are paired. However, because of the attractive forces due to ionic structures mentioned above, it seems quite reasonable that collision between a nitrogen atom and an alkyl chloride molecule should lead to a complex with long enough lifetime to permit the change in spin to occur. To explain the marked effect of HCl on the recombination of hydrogen atoms, a stable H.HCl complex has been postulated (17). Nitrogen atoms should be able to form collision complexes of this type more readily than hydrogen atoms because of both their greater electronegativity and their greater mass. For a collision complex to have a reasonable lifetime, interaction between different vibrational modes of the complex is necessary, and this is favored by closer spacing of the vibrational energy levels, i.e. by greater mass of the atoms concerned.

Of the electronegative atomic reactants that have been studied, nitrogen atoms appear to be the only ones for which the direct attack is favored over hydrogen abstraction. This is probably due mainly to the endothermicity of reactions of the type

$$RH + N \rightarrow NH + R$$

and the high exothermicity of the direct attack.

APPENDIX

STANDARD HEATS OF FORMATION ($\Delta H°_f$) OF GASEOUS COMPOUNDS AT 25°C. FROM ELEMENTS

Formula	Remarks	$\Delta H°_f$ (kcal.)	Formula	Remarks	$\Delta H°_f$ (kcal.)
H		52.089	CH_3Cl		−19.6
H_2		0	CN		94
Cl		29.012	HCN		31.2
Cl_2		0	C_2H_2		54.194
HCl		−22.063	C_2H_4		12.496
N		113.0	C_2H_5		26
N_2		0	C_2H_6		−20.236
NH		86	C_2N_2		73.60
C		171.698	C_3H_6		8.5
C	Graphite	0.	C_3H_7	*n*-Propyl	24
CH		142.1	C_3H_7	Isopropyl	18
CH_2	Singlet	66	C_3H_8		−23.5
CH_2*	Triplet	85	C_2H_3Cl		7.5
CH_3		32	C_2H_5Cl		−25.1
CH_4		−17.889	*n*-C_3H_7Cl		−31.1

Except as indicated below, the values were taken from National Bureau of Standards compilations (28, 29) or calculated from bond dissociation energies given by Steacie (38). For convenience, the temperature of reaction has generally been chosen as 25°C. For a few compounds, where values at 25°C. were not readily available, values for 0°K. have been used; the correction involved is less than the uncertainty in most of the values concerned.

$D(N_2)$: The high value, 9.76 ev., that is now generally accepted (cf. Ref. 8) has been used.

$\Delta H°_f(CN)$: Determinations of this quantity by several methods (4, 24, 27) indicate that a safe estimate is $\Delta H°_f(CN) = 94 \pm 2$ kcal.

$\Delta H°_f(CH_2)$, $\Delta H°_f(CH_2*)$: The values recorded for these quantities are uncertain (see Ref. 38).

$D(CH_2—H)$: Estimates by several methods (20, 21, 26, 36, 51) indicate that $D(CH_2—H) = 86 \pm 5$ kcal.

Opinions differ (20, 52) as to whether the singlet or triplet state of the methylene radical is the more stable. It has been assumed that $D(CH_2—H)$ applied to formation of methylene radicals in the singlet state and, as a rough estimate, that 19 kcal. of excitation energy (24) is required to reach the triplet state.

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THE MICROPORE FLOW OF H_2O AND D_2O THROUGH ACTIVATED CARBON RODS[1]

By M. E. Huber,[2] E. A. Flood, and R. D. Heyding

ABSTRACT

The flow rates of water adsorbed on activated charcoal have been measured at temperatures between −24°C. and +35°C. and compared with the flow rate of adsorbed D_2O at 25°C. In earlier papers a formula was presented which describes the micropore flow rate of adsorbed water as a laminar flow of liquid adsorbate under a high pressure gradient due to surface forces. Our results confirm this picture. From our flow data the relative viscosity of adsorbates can be calculated. Above 0°C. the viscosity of the adsorbate shows nearly the same temperature dependence as liquid water; below 0°C. the viscosity increases much more rapidly, but there is no sudden increase which could be ascribed to freezing of an appreciable fraction of the adsorbate at any particular temperature. The greater temperature coefficient of the adsorbate viscosity is consistent with a viscous flow of liquid films over a solid surface which exerts attractive forces on the liquid.

INTRODUCTION

It has been well established (1, 3, 9) that in the absence of appreciable absorption, the flow of gases through active carbons is a viscous flow with slip through the macropore system. The flow rate may be described by the well-known equation

$$[1] \qquad K = \frac{Q_{pv}}{\Delta p} = A\sqrt{\frac{T}{M}} + \frac{B}{\eta}\bar{p},$$

where Q_{pv} = flow rate in pv units,

$\bar{p}$ = mean of input and output pressures (mm. Hg),

A, B = constants,

M = molecular weight,

η = gas viscosity,

Δp = difference between input and output pressures.

From flow data for a gas such as helium the constants A and B can be evaluated and Equation [1] used to calculate flow rates of other gases of known viscosities at various temperatures, provided that the gases are not strongly adsorbed.

If a gas is strongly adsorbed the observed flow rates may be much higher than given by Equation [1]. Such increased flow rates have been attributed to flows through the micropore systems by (*a*) surface diffusion (2, 3, 4) and (*b*) laminar or viscous flow of liquid adsorbate. Previous work in this laboratory (8, 9) indicates that in the case of our carbon the second of these alternative mechanisms is the dominating one when the quantity adsorbed is at all large.

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If we assume that during the adsorption reaction the adsorbate and the adsorbent retain their own physical properties (equation of state) it can be shown (6, 7) that the adsorbate in order to be in equilibrium with the gas outside must have a volumetric mean pressure given by

$$[2] \qquad p_a = \int_0^p \frac{\rho_a}{\rho_g} dp = \left|\overline{\frac{\rho_a}{\rho_g}}\right| p;$$

p_a = volumetric mean pressure of adsorbate,
ρ_a = mean density of adsorbate,
ρ_g = gas density,
p = gas pressure.

Thus a small gas pressure difference across a carbon plug may give rise to a much larger pressure difference across the corresponding adsorbate. It has been shown (5) that these pressures actually exist and can be used to calculate dimensional changes of the solid with considerable accuracy (7).

Where gas densities are very low compared with liquid densities the flow rate of an adsorbate of uniform viscosity in micropore systems of uniform pore diameters is given by

$$[3] \qquad Q_m = -\frac{c}{\eta_a} \rho_a \frac{dp_a}{dz} = -\frac{c}{\eta_a} \frac{\rho_a^2}{\rho_g} \frac{dp}{dz}$$

or in integrated form

$$Q_m = -\frac{c}{L\eta_a} \int_{p_1}^{p_2} \frac{\rho_a^2}{\rho_g} dp = \frac{c}{L\eta_a} \left|\overline{\frac{\rho_a^2}{\rho_g}}\right| \Delta p,$$

where Q_m = flow rate in mass units,
C = constant (a function of pore dimensions),
η_a = viscosity of adsorbate (liquid viscosity),
L = length of carbon plug.

Assuming that the adsorbate has the viscosity of the corresponding liquid, it has been shown (9) that the micropore flow rates of benzene, ethyl chloride, diethyl ether, methanol, and water are described fairly well by Equation [3]. As a further check on the validity of Equation [3] we have measured the micropore flow rate of D_2O at 25°C. and the micropore flow rates of H_2O at temperatures from −24°C. to +35°C. The activated carbon rods or plugs through which the micropore flow rates were measured were similar to those used previously. We have also used carbon rods whose macropore systems were partially filled with a metal alloy, thus greatly increasing the relative contribution of the micropore flow to the total flow rate. Normally in measurements of the permeabilities of active adsorbents the observed flow is the total flow through both macropore and micropore systems. The "observed" micropore flow is obtained by calculating the macropore flow by means of Equation [1] and subtracting this calculated flow from the total. Evidently the smaller the relative contribution of the macropore flow the more accurately the micropore flow can be measured by such procedures. The experimental

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results to date, while largely confirming the validity of Equation [3], indicate that the temperature coefficient of the viscosity of adsorbed water is higher than that of liquid water. The results are consistent with laminar flow of liquid films in a surface force field.

Experimental results and relevant discussion are presented in what follows.

EXPERIMENTAL

Material

The activated carbon consists of very uniform, zinc-chloride activated, extruded, and calcined rods of 0.38 dm. diameter. They come from the same supply as the ones described in earlier papers (9, 12), the carbon being very similar to National Carbon Co. N19. We repeat their properties:

Helium density	2.22±0.05 gm. per cc.
Hg density	0.707±0.001 gm. per cc.
Void fraction	0.68
Void fraction at saturation assuming adsorbate has density of liquid:	
diethyl ether	0.24
water	0.30
BET surface nitrogen	1100 meters^2 per gm.

Properties of Single Plugs

Plug	Length	Macropores filled to	N_2 flow at 35.3°C.	N_2 flow reduced by filling to	Micropore flow reduced by filling to
26	1.00	0%	$K = 0.00209\bar{p} + 0.62$	—	—
23	0.417	(36%)	$K = 0.104$	6.4%	67%
28	0.535	39%	$K = 0.102$	11.9%	71%
29	1.001	53%	$K = 0.023$	3.3%	—

Plugs 23 and 29 were filled with alloy for 20 min. at 220°C. and 340 p.s.i., then molded into indium at 195°C. with 340 p.s.i. Plug 28 was filled under the same conditions except that it was filled under 370 p.s.i. and molded into indium under 1 atm. (breaking the vacuum). The degree of filling of the macropores is calculated from the uptake of alloy (based on a macropore void volume of 0.30). For plug 23 this figure (36%) is evidently too small. Presumably during the molding some indium must have been taken up. Column 4 gives the K values for the nitrogen flow. For the filled plugs, only the slip part of Equation [1] is given because the other term is very small and our measurements are all at low pressures (<50 mm. Hg). Before the filling with metal, the K values per unit length were the same for all three plugs within 10%. The values of the last column are based on the micropore flow of plug 26.

Flow Apparatus

Fig. 1 illustrates the apparatus used for measuring the flow rates of water vapor through charcoal. The procedures used in obtaining the flow rates of

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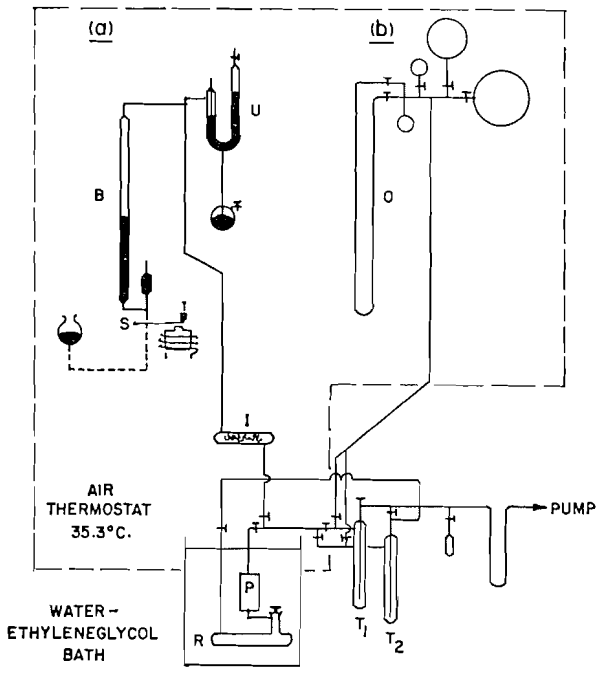

FIG. 1.

water vapor through plug 29 as well as the nitrogen flow rates through all of the plugs were essentially similar to those reported previously (12).

During the flow rate measurements for plugs 26, 23, and 28 the input sides of the carbons were exposed to saturated water vapor; this was done by keeping the reservoir R which contained liquid water at the same temperature as the plug. The gas flowing through the plug in the plug holder P was collected in one of the traps T. After a measured time, the trap was disconnected from the plug, and the amount of water in the trap determined in part (*b*) by expanding into a known volume and by reading the pressure on an oil manometer O. When the output pressure was zero, the traps were cooled with liquid nitrogen. For other output pressures, the traps contained a measured amount of water and were kept in a thermostat at the corresponding temperature. For a flow measurement under adsorption conditions, the plug was evacuated initially, equilibrated at the output pressure, and then the input pressure raised and Q_m or Q_{pv} observed till a constant value was obtained; for flow under desorption conditions, the plug was first saturated, the pressure reduced to a desired input pressure and equilibrated, the output pressure lowered, and Q_m observed as before.[3] The plug holder and the reservoir R were immersed in a water–ethyleneglycol bath, thermostated within ± 0.01°C. For temperatures below 15°C., the thermoregulator controlled a pump which

[3]*Thus adsorption state flow rates are initially too high when measured from the input side (plug 29) and desorption flows too low, and conversely when measured on the output side (plugs 26, 23, and 28).*

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circulates liquid from a reservoir cooled by mechanical refrigeration to a temperature a little below that desired in the thermostat. The nitrogen flows through the plugs were measured with the aid of part (*a*), Fig. 1.

The flow measurements for plugs 26, 23, and 28 were all reproducible within better than 5% while the more difficult measurements for plug 29 were usually reproducible within 10%. From time to time we repeated the nitrogen flow to make certain that no leaks had developed around the plug. Flow rates for plug 29 are given in *K* units while for plugs 26, 23, and 28, the flow rates are given in *pv* (mm. Hg×cc.) units per minute measured at 35.3°C.

Plug Holder

In runs with unfilled plugs the same type of holder was used as described previously (9, 12), the carbon rod being held between two funnel-shaped glass tubes and the sides surrounded with mercury, thus preventing gas flow around the carbon. When we used metal-filled plugs this holder was not satisfactory as the mercury amalgamates immediately with the low melting alloy in the plug. Fig. 2*a* illustrates the holder which was used in this case.

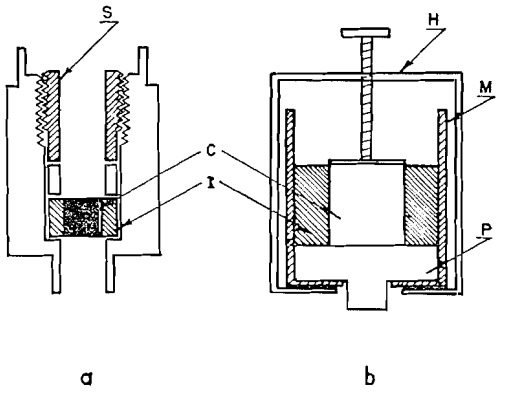

FIG. 2.

The carbon plug C is surrounded by a ring of indium I which fits precisely into the holder. By means of the screw S the indium, a very soft metal, is compressed and forms a tight seal. As indium picks up traces of mercury vapor very readily (11), the apparatus was kept free from mercury. The holder is connected with the glass system by glass to Covar seals. Fig. 2*b* shows the device used to make the indium ring around the plug. The carbon is held in the center of the cylinder by a screw. Then the whole is put in a bomb and indium is added. The bomb is evacuated overnight at 130°C. Then the temperature is increased to 190°C., the vacuum broken, and the desired nitrogen pressure applied for five minutes. The bomb is opened, the cylinder taken out, and after cooling down the piston is forced out.

The filling of the macropores with metal was carried out as follows. The plug was placed in a small test tube together with the Pb–Sn eutectic (61.8 Sn, 38.2 Pb, m.p. 183°C., *d*, 8.5 gm./cc.). The whole was placed in a bomb, which was evacuated overnight at 150°C.; then the temperature was slowly

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increased to 220°C. At this temperature nitrogen pressure from a tank was applied for 20 min. It was found that this time was enough to fill the plug uniformly, as longer exposures to the pressure gave no more increase in weight. After the pressure was released the bomb was opened rapidly and the still liquid content of the test tube poured onto a glass plate. By this procedure no metal adheres to the surface of the carbon, hence from the increase in weight the volume occupied by metal can accurately be calculated.

The adsorption isotherm of the carbon was measured in a conventional McBain system. We found that the isotherm of a metal-filled plug was the same as of an unfilled one.

RESULTS

In order to compare our experimental results with the theory underlying Equation [3], it is convenient to modify the equation by putting $\rho_a = x/V$, where x = grams adsorbed per gram of carbon and V = micropore volume per gram of carbon, and also by putting $\rho_g = pM/RT$ and $p = \alpha p_s$, where p_s is the saturation pressure. With these substitutions Equation [3] becomes

$$Q_m = \frac{c}{L\eta_a}\frac{RT}{V^2M}\int_{\alpha_2}^{\alpha_1}\frac{x^2}{\alpha}\,d\alpha$$

$$= \frac{c}{L\eta_a}\frac{RT}{V^2M}\left|\overline{\frac{x^2}{\alpha}}\right|\Delta\alpha,$$

or in pv units

$$Q_{pv} = \frac{c}{L\eta_a}\frac{R^2T^2}{V^2M^2}\left|\overline{\frac{x^2}{\alpha}}\right|\Delta\alpha, \qquad [3a]$$

and in K units

$$K = \frac{Q_{pv}}{\Delta p} = \frac{c}{L\eta_a}\frac{R^2T^2}{V^2M^2}\frac{1}{p_s}\left|\overline{\frac{x^2}{\alpha}}\right|. \qquad [3b]$$

When pv is measured at a constant temperature (35.3°C.), but the porous adsorbent is at various temperatures, Equation [3a] can be written

$$Q_{pv}' = \frac{c'}{\eta_a}\frac{T}{M^2}\left|\overline{\frac{x^2}{\alpha}}\right|\Delta\alpha, \qquad [3c]$$

where $c' = cR^2T_{35}/LV^2$.

Equations [3a], [3b], [3c] permit of a number of searching experimental tests of their validity. Thus according to Equation [3b] at a given temperature the flow rate K, for a given vapor, should vary with the mean value of x^2/α averaged over $\Delta\alpha$, as obtained from the plot of x^2/α as a function of α. Also for equal values of $|\overline{x^2/\alpha}|$, K values at 25°C. and 35°C. should be related as follows:

$$\frac{K_{25}}{K_{35}} = \frac{\eta_{35}}{\eta_{25}}\left(\frac{T_{25}}{T_{35}}\right)^2\frac{p_{s(35)}}{p_{s(25)}},$$

where η_{35} and η_{25} are the viscosities of the adsorbate at 35°C. and 25°C. respectively, $p_{s(35)}$ and $p_{s(25)}$ are the corresponding saturation pressures, and T_{35} and T_{25} are the absolute temperatures.

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While in the theory underlying these equations, the adsorbate layers are assumed to have the viscosity of the normal liquid, the "viscosity" of a Newtonian liquid in a strong attractive force field will be greater than that of the normal liquid and show a greater temperature dependence, such effects being the greater the thinner the liquid layer. Thus the adsorbate in the desorption state should have a viscosity somewhat closer to that of the normal liquid than the adsorbate in the adsorption state.

In the case of H_2O micropore flow, assuming that the adsorbate has the viscosity of liquid water, the ratio $K_{25}/K_{35} = 1.34$. Fig. 3 shows plots of K values for H_2O at 25°C. and 35°C. as functions of $\bar{\alpha}$ (i.e., of $(p_1+p_2)/2p_s$)

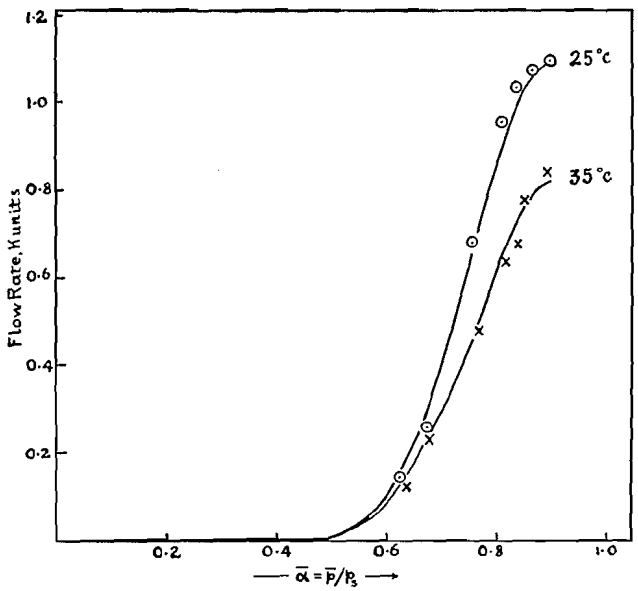

FIG. 3.

where $\Delta\alpha$ is 0.2 in each case. The solid lines are calculated from the observed K value at 25°C. and $\bar{\alpha} = 0.89$. The isotherm is used to calculate K at other values of $\bar{\alpha}$ and K_{25}/K_{35} is taken as 1.34. The experimental points are indicated by the crosses.

The agreement between the observed and calculated values is probably well within the experimental error since it is difficult to set and maintain $\Delta\alpha = 0.2$ exactly for each value of $\bar{\alpha}$.

While these equations are based on thermodynamic equilibrium between vapor and adsorbate and hence, strictly, can be valid only for infinitesimal $\Delta\alpha$, it is much easier experimentally to measure flow rates from $\alpha_1 = 1$ to $\alpha_2 = 0$ (i.e., from saturation to vacuum) than it is to set, maintain, and measure the slow flow rates for small values of $\Delta\alpha$. This procedure is a much more stringent test of the practical validity of these equations.

Since as shown by Coolidge (5) the adsorption isotherm of water vapor expressed as a function of the relative pressure, α, is the same over the tem-

perature range −30°C. to +30°C., then for $\Delta\alpha = 1$, $\overline{|x^2/\alpha|}$ has the same value in this temperature range. Accordingly, if our equations are valid under these conditions, we should have from Equation [3*c*]

$$\frac{Q'_{pv(T_1)}}{Q'_{pv(T_2)}} = \frac{\eta_{l(T_2)} \cdot T_1}{\eta_{l(T_1)} \cdot T_2}$$

where $Q'_{pv(T_2)}$ is the flow rate in *pv* units at the plug temperature T_2, the volumes being measured at some constant temperature (35.3°). $\eta_{l(T1)}$ is the viscosity of liquid water at T_1. This relation should hold over the temperature range −30° to +30°C., provided that the adsorbate does not freeze and has the viscosity of water.

In Table I the micropore flow rates for plug 28 are given at 25°C. and at 15°C. and their ratios compared for various values of $\Delta\alpha$ for both adsorption

TABLE I

MICROPORE FLOW RATES OF WATER VAPOR THROUGH PLUG 28 AT 25°C. AND 15°C.

	α_1	α_2	Q(25°C.)	Q(15°C.)	Q_{25}/Q_{15}	Q_{25}/Q_{15} calc.
Adsorption state	1	0.00	25.1	16.7	1.50	1.32
	1	0.50	23.5	15.2	1.55	1.32
	1	0.80	16.6	10.8	1.54	1.32
Desorption state	1	0.00	45.3	33.3	1.36	1.32
	1	0.80	17.3	12.6	1.37	1.32

and desorption states. The calculated curves are shown in Fig. 4 based on the adsorption flow rate for $\Delta\alpha = 0.2$.

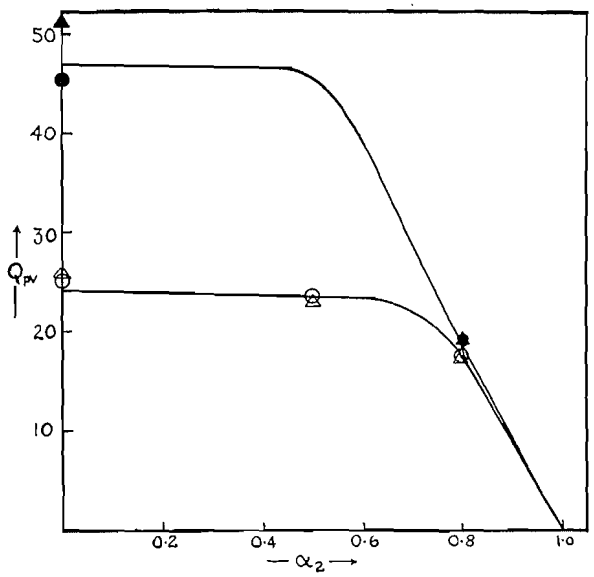

FIG. 4.

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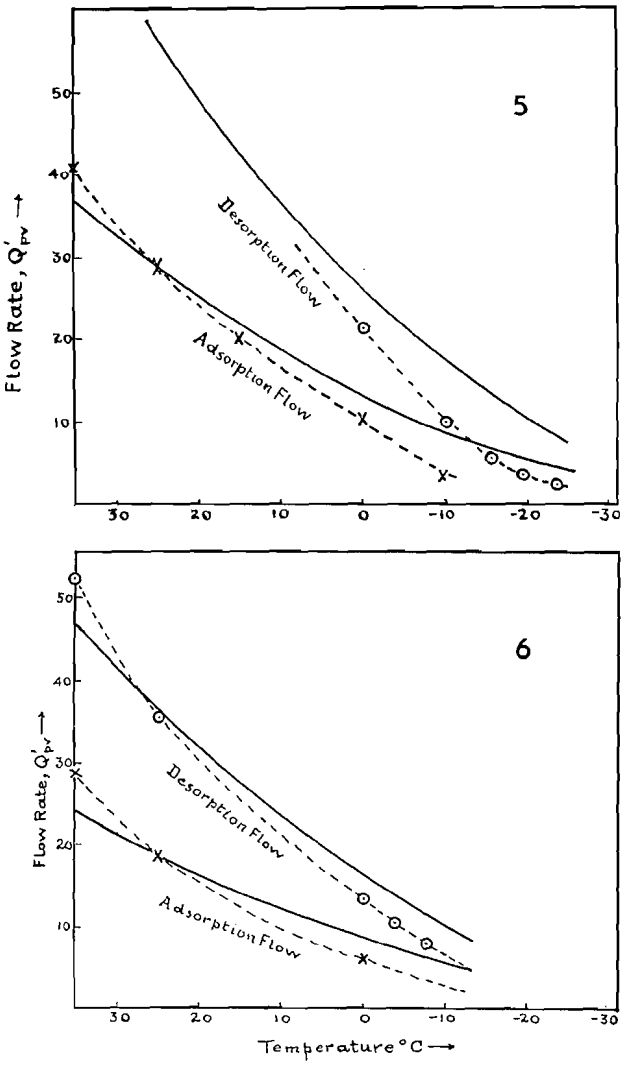

FIGS. 5 and 6.

Evidently Equation [3] is reasonably valid for $\Delta\alpha = 1$ as well as for $\Delta\alpha = 0.2$ or less.

In Figs. 5 and 6 observed values of $Q_{pv}'(\Delta\alpha = 1)$ for plugs 23 and 26 respectively for both adsorption and desorption states are plotted as functions of the temperature. The solid lines are calculated from the value of Q_{pv}' at 25°C. under adsorption conditions. If the equations are valid the ratios of the Q_{pv}' values for plugs 23 and 26 should be independent of temperature and that this is practically the case is shown by the data in Table II.

It will be noted that if the adsorption isotherm expressed as moles adsorbed (i.e. x/M) is the same for two gases, as is the case with H_2O and D_2O (cf.

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TABLE II

MICROPORE FLOW RATES OF H_2O THROUGH PLUG 26 (UNFILLED) AND PLUG 23 (METAL FILLED) AT VARIOUS TEMPERATURES WHEN $\alpha_1 = 1$ AND $\alpha_2 = 0$
(Values in brackets are interpolated)

Temp., °C.	Q(plug 23)		Q(plug 26)		Q_{23}/Q_{26}	
	Ads.	Des.	Ads.	Des.	Ads.	Des.
35.0	40.5		28.9	52.4	1.39	
25.0	28.8		18.5	35.5	1.57	
15.0	20.0					
0.0	10.5	21.6	6.43	13.58	1.63	1.59
−3.8		(16.8)		10.4		1.61
−7.7		(12.3)		8.0		1.54
−9.7		9.9				
−10.0	3*					
−15.4		5.5				
−19.2		3.9				
−23.6		2.56				

**Q not quite constant, rising slowly even after eight days. Highest observed value 2.9.*

TABLE III

MICROPORE FLOW RATES OF H_2O AND D_2O AT 25°C., PLUG 28, ADSORPTION STATE

α_1	α_2	Q_{H_2O}	Q_{D_2O}	Q_{H_2O}/Q_{D_2O}	η_{D_2O}/η_{H_2O}
1	0.00	25.1	18.2	1.38	1.23
1	0.80	16.6	12.3	1.35	1.23

Fig. 7), then at the same temperature the ratios of Q_{pv}' for such pairs are inversely proportional to the ratios of their liquid viscosities. In Table III the observed micropore flow rates of D_2O and H_2O are compared. Evidently the observed ratio is somewhat higher than the ratios of the normal viscosities of D_2O and H_2O. It may be remarked that it is easily shown that in order that the D_2O and H_2O isotherms be related as found in Fig. 7, the molar adsorption potential for D_2O must be higher than that of H_2O, and hence the ratio of the viscosities of the liquids in these surface fields greater than their ratio in the absence of such fields, i.e., greater than the ratio of the normal viscosities of D_2O and H_2O.

DISCUSSION

The experimental evidence presented above largely confirms the validity of the underlying theory and indicates that the adsorbate behaves essentially as a liquid film in a force field, and that at temperatures above 0°C. the adsorbate viscosity is essentially that of the normal liquid. The experimental evidence indicates that the integrated equation is also valid even for the range $\alpha_1 = 1$, $\alpha_2 = 0$, i.e., $\Delta\alpha = 1$.

The theory underlying the flow equation is based on the assumption that equilibrium, as between adsorbate and vapor, exists everywhere throughout the flow path. Thus the basic equation is

$$-Q_{pv} = A\sqrt{\frac{T}{M}}\frac{dp}{dz} + \frac{B}{\eta_g}p\frac{dp}{dz} + \frac{c}{\eta_1}\frac{\rho_a^2}{\rho_g}\frac{dp}{dz},$$

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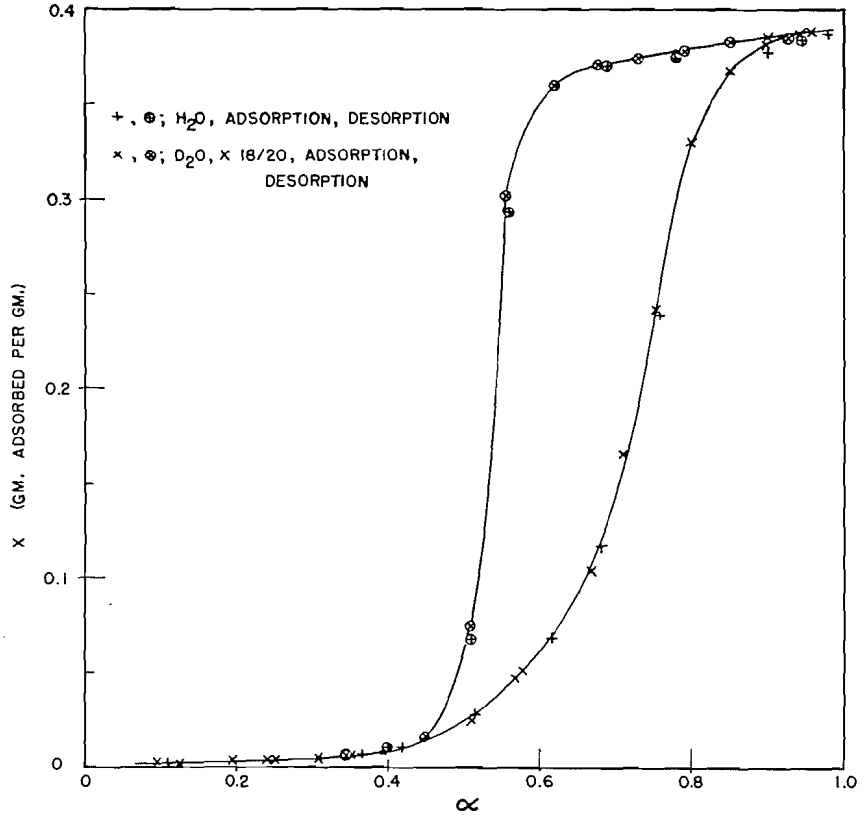

FIG. 7.

where η_g is the gas viscosity, η_l the liquid viscosity, etc. The first two terms of the right-hand member of the equation apply to the macropore system, and the third term to the micropore system. For small B and p the integrated form may be written

$$Q_{pv} = \frac{A}{L}\sqrt{\frac{T}{M}}\cdot p_s + \frac{c}{L\eta_l}\left|\frac{\overline{\rho_a^2}}{\rho_g}\right| p_s.$$

It may appear very surprising that this equation should hold even approximately, since at the low surface coverages near the effluent end of the rod where $p \to 0$, the traction of the adsorbed layer over the solid surface must be very different from that between water layers. Thus at first sight one might expect little direct correlation between liquid viscosity and flow rate when $\Delta\alpha = 1$.

While mathematically the integration carried out above is equivalent to treating the two pore systems as though they were independent, these systems are not physically independent. In the case of two physically independent systems the gas pressure gradient in the macropore system, neglecting the small Poiseuille term, would be linear, while the equilibrium gas pressure gradient corresponding to the micropore flow would be quite different conforming to

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the condition that $(c/\eta_l)(\rho_a^2/\rho_g)(dp/dz)$ on the input and output ends be the same, i.e., to constancy of Q_m (micropore). For macropore and micropore flows, the corresponding "equilibrium" gas pressures expressed as fractions of saturation, or α, are shown in Fig. 8 as functions of the distance z along the plug. As both systems are closely interconnected everywhere, only one gas pressure gradient can exist. Thus the form of $\alpha(z)$ for the actual system will lie somewhere between the macropore and micropore curves shown, depending on the relative permeabilities of the two pore systems. Evidently the flow through

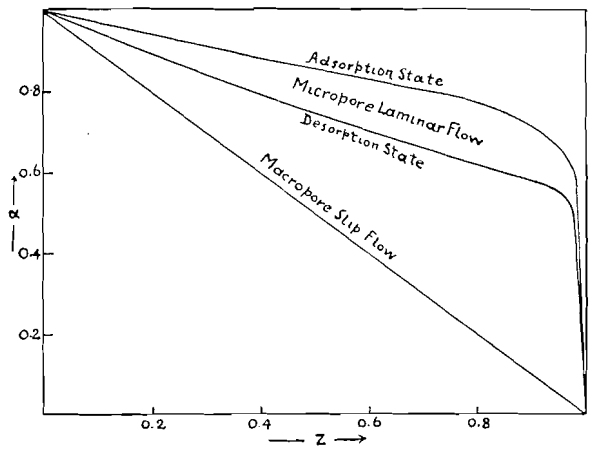

FIG. 8.

either one of the pore systems is not constant along the flow axis. For the case illustrated relatively more water flows through the micropores on the input side than on the output side. If ρ_a were constant along the flow axis, as would be the case if the micropore system were liquid filled from end to end, and quasi-equilibrium at the two ends maintained by surfaces of different curvatures (a model desorption state) the micropore flow would be relatively greater on the output side.

Fig. 8 shows that for micropore flow, when $\alpha_1 = 1$ and $\alpha_2 = 0$, i.e., from saturation to vacuum, the whole carbon is nearly saturated (92% and 88% saturated for desorption and adsorption states, respectively). Thus the steady state is reached much sooner for desorption flow than for adsorption flow. At $-10°$C. the steady state of flow under desorption conditions was reached in a day but for adsorption flow even after eight days the flow rate was not quite constant.

That the flow should be inversely proportional to liquid viscosity, in spite of the fact that at the low pressure end of the plug the theoretical model cannot be even approximately valid, is made clear from Fig. 8. Evidently 95% of the length of the flow path is nearly saturated, practically all of the equilibrium gas pressure drop occurring over the last 5% of the length. If the viscosity in the last 5% were twice as large as in the rest of the plug, the pressure drop over the 5% must be twice as large as shown in Fig. 8. Thus the

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pressure gradient which forced the adsorbate through 95% of the length of the carbon has, in this latter case, to force it through 97.5% of its length. The total effect on the flow rate is less than 3%. Evidently the apparent viscosity of the adsorbate at the effluent end of the carbon rod does not influence the flow rates materially when the influent end is saturated.

If the micropore flow rates are much too high for equilibrium between adsorbate and gas pressures (input and output) to be even approximately attained (e.g. a very short plug or thin diaphragm) serious departures from the above equations are to be expected. In such cases the density of the adsorbent at the effluent end will be much too great and the adsorbate pressure gradient too small, the former leading to larger Q_m values than calculated, the latter to smaller values. Such high flow rates are also liable to cause a temperature gradient across the plug and lead to lower Q_m values.

Finally in Fig. 9 apparent adsorbate viscosities are plotted as functions of temperature. Evidently, there is no evidence of freezing of any considerable part of the adsorbate. Since in the desorption state part of the adsorbate is

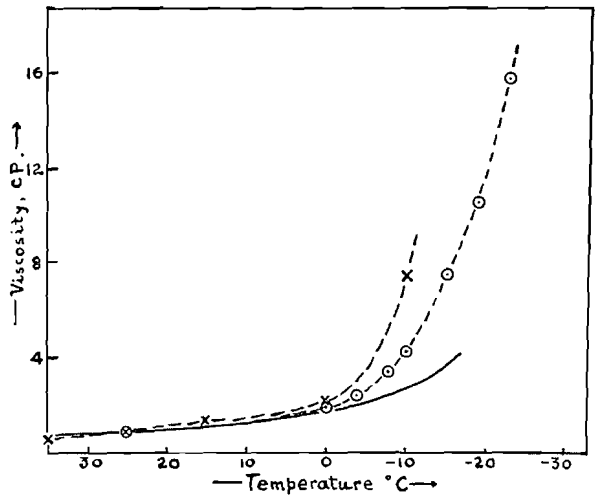

FIG. 9.

under a net negative pressure, one might have expected more evidence of solidification for desorption state flow. However, no such evidence can be adduced from the data. Assuming (10) that one may write $\eta = B \exp(E_{vis}/RT)$, the mean "activation energy", E_{vis}, of viscous flow for liquid water in the interval +35°C. to 0°C. is of the order of 4.3 kcal. For desorption flow E_{vis} is of the order of 4.9 kcal. while for adsorption flow it is about 6.0 kcal. If the "potential" of the surface regions containing the "liquid" films is 3 or 4 times ΔE_{vis}, i.e. similar to the relation of E_{vis} to E_{vap} for normal liquid water, the surface potential is about 5 kcal. per mol. adsorbed for the adsorption state and about 2 kcal. for the desorption state. These surface "energies" are about what one might expect for such carbons.

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The evidence presented above indicates that for our carbon rods the micropore flow rate of water can be described semiquantitatively by the equation

$$Q_m = \frac{c}{L\eta_1}\int_{p_2}^{p_1} \frac{\rho_a^2}{\rho_g}\, dp.$$

The viscosity of the adsorbate appears somewhat higher than that of liquid water and the temperature coefficient of the adsorbate viscosity greater. The equation appears to describe the relative flow rates for various values of $\int_{p_2}^{p_1} \rho_a^2/\rho_g\, dp$ at constant temperature more accurately than it describes the relative flow rates at constant $\int_{p_2}^{p_1} \rho_a^2/\rho_g\, dp$ values and varying temperatures. The variation of the viscosity of the adsorbate is qualitatively in accordance with theoretical considerations.

It is, of course, to be emphasized that the micropore flow mechanisms discussed here are not applicable to systems of micropores of molecular dimensions as no laminar flow can take place in pore systems of only one or two molecular diameters. However, the equations should be reasonably valid as applied to the flow of five or more molecular layers and hence should be reasonably valid as applied to the flow of small molecules adsorbed in micropore systems of almost constant pore sizes of 10 Å diameter or more. In the case of micropore systems of platelet structure, the distance between platelets might be somewhat less than 10 Å and still be consistent with liquid viscous flow.

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THE CHEMICAL STABILITY OF THE *S*-METHYL XANTHATES OF SOME SIMPLE ALCOHOLS[1]

By D. L. Vincent[2] and C. B. Purves

ABSTRACT

n-Octadecyl *S*-methyl xanthate, m.p. 38–39°, and *n*-hexadecyl *S*-methyl xanthate, m.p. 28–28.5°, were prepared for the first time, and were used to study the behavior of the *S*-methyl xanthate group toward reagents commonly used in research on carbohydrates. Although stable to some conditions of acetylation, hydrolysis, and methanolysis, the *S*-methyl xanthate group was destroyed by all methylating agents tried, with the exception of nitrosomethylurethane. The latter reagent converted a sodium xanthate salt in high yield to the *S*-methyl ester. Octadecyl and hexadecyl *S*-methyl xanthates when oxidized with hydrogen peroxide yielded crystalline substances of composition $C_{20}H_{40}O_4S_2$ and $C_{18}H_{36}O_4S_2$, respectively, whose structures were not determined. These substances each contained three additional oxygen atoms. Various attempts to estimate the *S*-methyl xanthate group by oxidation with bromine or periodic acid, or by reduction to methyl iodide, were unsuccessful.

INTRODUCTION

As a preliminary to research on xanthates of carbohydrates, it seemed desirable to investigate some simple, crystalline derivative of the xanthate group that was more stable than a free xanthic acid or its alkali salt toward reagents frequently used in carbohydrate chemistry. Xanthate-*S*-methyl esters at once came into consideration, because they could be formed in high yield by the action of methyl iodide on a suitable salt. The term "xanthate ester" referred to a double ester such as $C_2H_5OCSSC_2H_5$, whose formal name was ethyl ethoxymethanethionothiolate, but which could be more clearly described as *O*-ethyl *S*-ethyl xanthate (6).

Simple xanthate esters were usually high-boiling liquids, and of the *S*-methyl compounds only eight were reported as crystalline. All eight were derived from aromatic, hydroaromatic, and terpene alcohols, and their carbon skeletons were unnecessarily complicated for the purpose in view. Nevertheless, the *S*-methyl xanthates of benzyl and hexahydrobenzyl alcohol, and of menthol, were prepared for reference purposes. Whitmore and Simpson's modification (25) of the long-neglected Zeise (27) "one-step" process employing the alcohol, solid sodium hydroxide, carbon disulphide, and later methyl iodide, was used. The melting point of the hexahydrobenzyl derivative was confirmed as 16.5°, apparently the value given by Aleksandrovich (1), and not as 165°, as misquoted by Chemical Abstracts and British Chemical Abstracts. The same general method was used to synthesize several *S*-methyl xanthates of normal aliphatic alcohols in 60–80% yield. It transpired that the octyl derivative was a liquid, and that the *S*-methyl xanthates of *n*-hexadecyl (cetyl) and *n*-octadecyl (stearyl) alcohol were crystalline solids whose melting

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points were in a practical range. Most of the subsequent work was carried out on the higher-melting octadecyl derivative, but even in this series recrystallizations of the wax-like solids had to be performed in a room at 8°, and often occasioned serious losses in yield.

There are several assumptions in the literature that a sodium xanthate salt in presence of an excess of nitrosomethylurethane yielded the methyl ether of the parent alcohol. When a solution of sodium octadecyl xanthate (80–87% purity) in methanol was mixed with a fivefold molar excess of the above reagent, *O*-octadecyl *S*-methyl xanthate, and not the expected methyl ether of octadecanol, was swiftly formed in quantitative or nearly quantitative yield. Diazomethane was probably the actual methylating agent because the solution became yellow as the nitrosomethylurethane was added. In the same way, crude potassium benzyl xanthate gave benzyl *S*-methyl xanthate, although manipulative and other difficulties greatly reduced the yield.

Table I summarizes experiments on the stability of various *S*-methyl xanthates toward alcoholic sodium hydroxide. Distinct end points to phenol-

TABLE I

SAPONIFICATION OF *O*-OCTADECYL *S*-METHYL XANTHATE IN 90% AQUEOUS ETHANOL[a]

Conditions	Hydrolysis, %	
	NaOH, 1.2 *N*	NaOH, 0.09–0.11 *N*
1 hr. near 20°	19.9	4.1
48 hr. near 20°	78.9	75.0
1 week near 20°	161	175
15 min. at reflux[b]	73.7, 68.8	68.7
30 min. at reflux	92.5, 89.3	92.1
1 hr. at reflux[c,d]	99.7, 102	99.2, 98.5

[a]*The pure samples, 0.19–0.32 gm., were dissolved in 5 ml. or 10 ml. of 1.2 N alkali, or in 50 ml. of the 0.1 N alkali.*

[b]*When heating was preceded by 90 min. at 20° and with 0.8 N potassium hydroxide, the hydrolysis of benzyl S-methyl xanthate was 101, 102%.*

[c]*Hydrolysis of benzyl S-methyl xanthate, 91, 100, 84%. End points indistinct.*

[d]*Hydrolysis of menthyl S-methyl xanthate 80–100%. End point very indistinct.*

phthalein were obtained when saponifications of *O*-octadecyl *S*-methyl xanthate were titrated with standard hydrochloric acid, but those given by benzyl *S*-methyl xanthate were somewhat transitory. The assumption that complete hydrolysis corresponded to the reaction $R—OCSSCH_3 + 2NaOH \rightarrow R—OH + Na_2CO_2S + CH_3SH$ usually gave good results when the solution was boiled, but not when saponifications were carried out at room temperature and failure to expel methyl mercaptan led to an overconsumption of alkali. Decinormal alkali was almost as effective as *N* sodium hydroxide. In one experiment a 97% yield of nearly pure octadecanol was recovered, and in others the recoveries of benzyl alcohol and menthol were both about 70%. On the other hand, boiling 25% aqueous sodium hydroxide left over 95% of the *O*-octadecyl *S*-methyl xanthate unchanged after two hours. These results supplemented McAlpine's observation (17, 18) that concentrated alcoholic potassium

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hydroxide caused complete hydrolysis of menthyl *S*-methyl xanthate in 12 to 18 hr., but that this substance, as well as its bornyl analogue, was stable to boiling 40% aqueous potassium hydroxide. Lieser and Leckzyck (16), however, found that an *S*-methyl xanthate of methyl glucoside was readily hydrolyzed by aqueous alkali. To sum up, it appeared likely that xanthate esters resisted decomposition by aqueous alkali when they were highly insoluble in this medium, but in other circumstances were far less stable to alkali than their sodium salts. Neither the ester nor the salt was likely to survive the conditions usual for methylating carbohydrates with dimethyl sulphate and alkali. Deacylation with *N* aqueous alcoholic ammonia might be possible without disturbing *S*-methyl xanthate groups, because the octadecyl derivative was stable to this reagent at room temperature for days. Nevertheless, Laakso (14) and earlier workers found that xanthamides (thiourethanes) resulted when xanthate esters were treated with aqueous or alcoholic ammonia. *O*-Octadecyl *S*-methyl xanthate was also nearly stable to pyridine at room temperature, although decomposition was extensive when the solution was heated (17, 18).

Lieser and Leckzyck (16) remarked that their *S*-methyl xanthate of methyl glucoside was surprisingly stable to boiling dilute hydrochloric acid. This contrast to the instability of xanthate salts toward acid was emphasized by the behavior of *O*-octadecyl *S*-methyl xanthate, which was not appreciably affected by boiling 6 *N* hydrochloric acid for three hours, and was recovered in high yield after exposure to the 43% acid for 24 hr. at 0°. Neither heating under reflux, nor in a sealed tube at 120°, with 3% methanolic hydrogen chloride caused appreciable change within three days, but decomposition was extensive when the temperature was raised to 160° during six days. This decomposition might have originated in thermal effects, because the pure xanthate ester decomposed vigorously and exothermally at 180–190°. By analogy with the behavior of other xanthate esters, the heating might have produced either a modification that was more stable thermally (6, 17, 18) or an isomerization to a dithiocarbonate, RSCOSR (12, 14), or the well-known Chugaev breakdown to an unsaturated hydrocarbon (2, 8, 25). The results in general suggested that the *S*-methyl xanthate group was reasonably stable to conditions often used for the hydrolysis and methanolysis of carbohydrates. This stability extended to acetylation or acetolysis with acetic anhydride and zinc chloride, as Lieser and Leckzyck (16) were aware.

A few experiments on the stability of *O*-octadecyl *S*-methyl xanthate toward heavy metals and their salts were carried out with the object of discovering mild conditions for dexanthation. When an alcoholic solution of the ester was heated under reflux with silver oxide or silver carbonate for at least one hour, octadecanol was formed together with a considerable amount of lower-melting material. Silver nitrate and mercuric acetate promoted chemical change at room temperature, but the major product was not octadecanol; cadmium carbonate failed to react with an ether solution of the xanthate within two weeks. Lieser and Leckzyck (16) employed silver or mercury salts to recover methyl-α-glucoside from its *S*-methyl xanthate, and their use in removing

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sulphur from other types of organic compounds is well known. A solution of thallous ethylate in dry benzene reacted readily with *O*-octadecyl *S*-methyl xanthate, giving a high yield of octadecanol and a black precipitate of thallium sulphide (or sulphides) within 12 hr. at room temperature. These experiments showed that any *S*-methyl xanthate groups present in a carbohydrate would be removed during methylation with silver oxide and methyl iodide, or with thallous ethylate followed by methyl iodide (21). It might, however, prove possible to remove such groups without disturbing any acetyl groups in a partly acetylated substance.

Some years ago Fletcher (11) found that *O*-ethyl *S*-(tetraacetyl-D-glucopyranosyl)-xanthate was desulphurized in high yield to tetraacetyl-1,5-anhydro-D-sorbitol when boiled in alcohol with Raney nickel. The same reagent

$$C_2H_5OCS_2—C_{14}H_{19}O_9 \rightarrow C_{14}H_{20}O_9$$

enabled Baddiley (4) to obtain phenylethane from methyl phenyl dithioacetate

$$C_6H_5CH_2CS_2CH_3 \rightarrow C_6H_5CH_2CH_3.$$

These results suggested that methane and octadecanol might be produced in a similar way from *O*-octadecyl *S*-methyl xanthate. The product, however, consisted of only 50–65% of octadecanol (m.p. 58°), and a white wax melting at 28–31.5° which could not be adequately purified by recrystallization, and whose relative amount increased to about 60% when the desulphurization was carried out at room temperature. The substance was a mixture which might have contained a little octadecyl methyl ether (m.p. 30–31°).

Although Delépine (9) observed that simple xanthate esters often oxidized spontaneously in air with the evolution of light and fumes, and were chemiluminescent, Billeter and Wavre (5) were apparently the only workers to identify products from a similar oxidation. They found that in presence of aqueous ammonia *O*-methyl *S*-methyl xanthate absorbed oxygen quickly and that sulphuric, sulphurous, and thiosulphuric acids were formed; *O*-ethyl *S*-ethyl xanthate yielded *O*-ethyl *S*-ethyl thiocarbonate in the same circumstances. On the present occasion, *O*-octadecyl *S*-methyl xanthate was oxidized with an excess of 30% hydrogen peroxide, an agent often used to prepare sulphones from thioethers. The product consisted of a white, crystalline substance whose composition, $C_{20}H_{40}O_4S_2$, indicated that three oxygen atoms had been added to the original xanthate molecule with the retention of both sulphur atoms. The substance was stable to acid and when saponified yielded octadecanol, hydrogen sulphide, and no sulphate ion. A similar oxidation of *O*-hexadecyl *S*-methyl xanthate yielded a crystalline compound, $C_{18}H_{36}O_4S_2$, also containing three extra oxygen atoms, but a preliminary oxidation of benzyl *S*-methyl xanthate resulted in a mixture of products including benzyl alcohol. A detailed examination of these interesting oxidations was deferred.

Some unsuccessful attempts were made to determine the *S*-methyl xanthate group by titrating an acidified solution of the octadecyl derivative with potassium bromide – potassium bromate, essentially as described by Siggia and Edsberg (22) for the oxidation of thioethers to sulphoxides. Both sulphur

atoms in the xanthate ester, however, were oxidized beyond the sulphoxide stage to an extent depending on the conditions, and the end point was indistinct. Liquid bromine readily oxidized octadecyl *S*-methyl xanthate to a white wax which contained neither sulphur nor halogen, and which was neither stearaldehyde nor stearic acid. Oxidations of the *S*-methyl xanthate with paraperiodic acid (another reagent of value in carbohydrate chemistry) also proceeded to an indefinite end point and failed to provide a basis for an analytical method. Several attempts were made to devise a method of analysis for the methylthio group (—SCH_3) in xanthate-*S*-methyl esters by cleavage to methyl iodide with constant-boiling hydriodic acid. Use was made of the Vieböck and Schwappach (23) method for methoxyl groups, in which the methyl iodide was absorbed in a solution of bromine, and of the Kirpal–Bühn (13) modification with pyridine as the absorbing agent. This modification was particularly suitable for substances containing sulphur. Both procedures, however, failed to account for more than a small fraction of the methylthio group, even when the boiling with hydriodic acid was prolonged for several hours. This result explained why Lieser and Leckzyck (16) were able to determine the methoxyl content of a xanthate-*S*-methyl ester of methylglucoside without much interference from the methylthio unit. In an earlier article (15), however, Lieser attempted to determine the methylthio group in a supposed cellulose xanthane-*S*-methyl ester by the same procedure, and attributed the unexpectedly low result to the occurrence of side reactions during the preparation of the ester.

EXPERIMENTAL

Materials

At room temperature, the solubilities of octadecanol in ligroin (b.p. 30–50°), benzene, acetone, ethanol, methanol, and ethanol–water (3:1) were approximately 1.25, 3.85, 2.2, 1.7, 0.7, and 0.2% respectively; well-formed leaflets were obtained from ligroin, but the crystal habit deteriorated progressively through the above list of solvents. Both octadecanol and hexadecanol were purified from ligroin. Absolute ethanol, methanol, and ether were purified by standard methods. The *S*-methyl xanthate of benzyl alcohol was prepared by Whitmore and Simpson's method (25) employing solid sodium hydroxide, and the product, isolated in 70% yield, melted correctly at 28.5–29.5° (20). The same general method was used, apparently for the first time, in the preparation of the *S*-methyl xanthates of hexahydrobenzyl alcohol and of menthol, although xanthation occurred somewhat less readily in the latter case. Yields were 30% and 32%, and melting points were correct at 16–17° (1) and 38.5–39° (8), respectively. Determinations of sulphur were made either by the semimicro Carius method, or by the method of Waters (24), which employed bromine and nitric acid at atmospheric pressure as the oxidizing agent.

O-Hexadecyl S-Methyl Xanthate

Pure hexadecanol, 36.3 gm. (0.15 mole), was dissolved in 200 ml. of reagent grade carbon disulphide contained in a 500-ml. three-necked flask fitted with a mercury-sealed stirrer and a reflux condenser. Then 6 gm. (0.15 mole) of pul-

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verized sodium hydroxide was quickly added, with continuous stirring, and was washed down with 50 ml. more of carbon disulphide. The reaction was exothermic, and a heavy, pale yellow gel formed within 10 min. After the mixture had been kept overnight, 37.4 ml. (0.60 mole) of methyl iodide was added in portions, with stirring, and by the next day the gel had been completely replaced by a pale yellow liquid containing a white precipitate of sodium iodide. After dilution with an equal volume of ether and after filtration, the liquid was evaporated under reduced pressure, finally in a vacuum desiccator. The yellow liquid, 50.2 gm. (100.5%), solidified to a pale yellow solid melting at 24–25° after remaining in a cold room for some time.

The product was twice recrystallized from a large excess of ethanol, each time in three or four crops, the yield of nearly pure white crystals being 40 gm. A third, similar crystallization gave a first crop of 27.2 gm. (54%) with the final melting point of 28–28.5°, and the small sample for analysis was recrystallized once more before being dried over phosphorus pentoxide in an evacuated desiccator kept in the cold room. Found: C, 64.7, 64.6, 64.9; H, 10.6, 10.9, 11.0; S, 20.0, 19.1%. Calc. for $C_{18}H_{36}OS_2$: C, 64.8; H, 10.9; S, 19.3%.

The 250 ml. of carbon disulphide used as the reaction medium could be replaced by a somewhat larger volume of ether.

Crude Sodium Octadecyl Xanthate

Pulverized sodium hydroxide, 3.2 gm. (0.08 mole), dry ether, 280 ml., and pure octadecanol, 21.6 gm. (0.08 mole), were stirred together in a flask equipped as described above. Although the octadecanol failed to dissolve completely, the stirring prevented a solid cake from forming. The thick suspension broke down immediately 9.6 ml. (0.16 mole) of carbon disulphide was added; the solution became yellow and the yellow xanthate salt gradually formed. After six hours of stirring and gentle warming, a further 9.6 ml. of carbon disulphide was added and the mixture was kept overnight. The salt was recovered on a filter and when dried in the air appeared as pale yellow crystals weighing 27.3 gm. (92.6%).

Following the procedure of DeWitt and Roper (10), the salt was dissolved in hot acetone, the solution filtered to remove 2 gm. of insoluble material, and then slowly diluted with benzene to cause reprecipitation. After a second purification, in which petroleum ether replaced benzene as the precipitating agent, the salt, now white, was dried in a vacuum desiccator containing phosphorus pentoxide, activated charcoal, and paraffin wax. Yield, 19.1 gm. (65%). Found: S, 15.4 (hypobromite method), 15.0% (Carius). Although white, the salt gave a very turbid solution in 4% aqueous sodium hydroxide and was obviously impure. An attempt at recrystallization from warm ethanol caused continual decomposition, since the clear solution rapidly became turbid. Finally, the salt was dissolved in an excess of acetone, the solution was filtered and diluted with about 10 volumes of pentane. Next day the white crystals were recovered and dried in a vacuum desiccator. Found: S, 14.8, 15.1 (Carius); Na, 4.74, 5.15% (sulphated ash); "iodine equivalent", 294. Calc. for $C_{19}H_{37}OS_2Na$: S, 17.4; Na, 6.24%; "iodine equivalent", 344. The iodine equivalent was obtained by titrating a weighed sample of the salt, dissolved in aqueous ace-

tone, with 0.1 *N* iodine, using a small layer of ether or carbon tetrachloride to determine the end point. The results were calculated according to Whitmore and Lieber (26) as milligrams of iodine per gram of xanthate salt. All the analyses showed that the sodium octadecyl xanthate had a purity of only 80 to 87%, but no means of purifying it further could be found.

O-Octadecyl S-Methyl Xanthate

(*a*) Octadecanol, 40.5 gm., was stirred in a flask (equipped as described above) with 250 ml. of carbon disulphide for several hours until solution was complete. When 6 gm. of pulverized sodium hydroxide was added with stirring, the heavy, pale yellow precipitate of the xanthate salt formed almost immediately, and one day later 37 ml. of methyl iodide was added. After the mixture had been gently warmed for a short time, and then allowed to stand for two days, an equal volume of ether was added to bring about a better separation of the sodium iodide.

The filtrate and washings when evaporated under reduced pressure, finally in a desiccator, left 48.1 gm. (89%) of a pale yellow solid melting at 37.5–38°. Recrystallization from 300 ml. of ethanol yielded four crops, of which the first two, 32.1 gm. (60%), melted at 37.5–38.5° and at 36–37°, respectively. The third and fourth crops, 8.6 gm., melting near 53°, were largely octadecanol. A sample of the purest material after three more recrystallizations from ethanol melted at 38–39°. Found: C, 66.5, 66.5; H, 11.0, 11.0; S, 17.9, 17.7%; mol. wt. (Rast), 388, 352. Calc. for $C_{20}H_{40}OS_2$: C, 66.6; H, 11.2; S, 17.8%; mol. wt., 360. The volatility of octadecyl *S*-methyl xanthate in steam, although slight, exceeded that of the parent octadecanol. When a 5 gm. sample of the ester was slowly heated, a thermometer being inserted directly into the pale yellow melt, a vigorous reaction occurred at 180–190° and the temperature increased to about 290°. Only a few drops of distillate were obtained at 315°, and the still residue on cooling separated into nearly equal amounts of a white solid and a pale yellow liquid. Both dissolved in ether, but neither was examined further.

(*b*) The same ester was also obtained in good yield by the action of methyl iodide on the sodium octadecyl xanthate isolated above.

Nitrosomethylurethane and Sodium Octadecyl Xanthate

A clear solution of the crude sodium salt described above, 1 gm. (2.7 mM.), in 100 ml. of absolute methanol was placed in a 500-ml. three-necked flask fitted with a mechanical stirrer, a thermometer, and a dropping funnel. Nitrosomethylurethane, 1.79 gm. (13.5 mM.), dissolved in 20 ml. of absolute methanol, was added dropwise at 3–5° during 20 min. After about five minutes a white foamy solid appeared on the surface of the solution, and increased in amount until the nitrosomethylurethane had all been added. Two hours later, when the temperature had risen to 15°, the solid was separated, was washed with a little absolute methanol, and was dried over phosphorus pentoxide in a vacuum desiccator. Concentration of the filtrate yielded a second crop, and a third was obtained by diluting the final mother liquor, 20 ml., with 250 ml. of water. The first two crops, totalling 0.87 gm. or 89%, melted at 36–38.5°, and

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two recrystallizations from ethanol failed to alter this value significantly. A mixed melting point with authentic octadecyl *S*-methyl xanthate was not depressed. Found: S, 17.6, 17.9%. Calc. for $C_{20}H_{40}OS_2$: S, 17.8%.

Alkali and S-Methyl Xanthates

(*a*) *Alcoholic Sodium Hydroxide*

The data were summarized in Table I. In order to recover the white precipitate which persisted throughout the saponification, which in this case was for one hour under reflux, the final mixture was evaporated to dryness. Extraction with boiling ether removed 97% of the calculated amount of octadecanol as a white solid melting at 55–57° and yielding the corresponding phenylurethane with the correct melting point of 79.5° (3). A 5.96 gm. sample of benzyl *S*-methyl xanthate, when boiled for 90 min. with 75 ml. of 1.2 *N* sodium hydroxide in 90% ethanol, yielded 2.16 gm. of redistilled benzyl alcohol (67%) from which a phenylurethane with the correct melting point of 77–78° was prepared.

The recoveries of octadecyl *S*-methyl xanthate, m.p. correct at 37–38°, were about 99% both from boiling 25% aqueous sodium hydroxide and from *N* 95% aqueous alcoholic ammonia at room temperature. Over 75% was recovered by evaporating a solution in pyridine which had stood for one week and by recrystallizing the residue from ether.

(*b*) *Thallous Ethylate*

Octadecyl *S*-methyl xanthate, 0.299 gm. (0.83 mM.), was dissolved at 5–10° in 25 ml. of a 0.095 *N* solution (1.9 mM.) of thallous ethylate in pure, dry benzene. Within a few seconds, the solution became yellow and turbid, and after a few minutes, deep brown. The reaction was perhaps one-third complete in 70 min. After the solution had been kept for 12 hr. in the dark, 50 ml. of 0.099 *N* hydrochloric acid and 20 ml. of methanol were added to decompose the remaining thallous ethylate, and the excess acid was back-titrated to a phenolphthalein end point with standard sodium hydroxide. The consumption of thallous ethylate was 1.63 mM., or 1.99 moles per mole of the xanthate ester.

In another experiment, 0.608 gm. (1 mM.) of *O*-octadecyl *S*-methyl xanthate was kept for 12 hr. in the dark with 50 ml. of the thallous ethylate solution. The mixture was filtered on sintered glass, and the black residue, which evolved hydrogen sulphide when treated with acid, was probably thallium sulphide. The clear, nearly colorless filtrate, which soon became turbid, when evaporated under reduced pressure gave a yellow brown solid. A solution of this solid in ether, when clarified by filtration and evaporated, left 0.64 gm. (106%) of near-white crystals with an unpleasant odor. When recrystallized from pentane, white leaflets melting at 56–57.5° were obtained, and from them a phenylurethane melting at 78–78.5°. The melting points recorded for octadecanol and its phenylurethane were 60° and 79.5° (3) respectively.

Acid and Octadecyl S-Methyl Xanthate

(*a*) *Hydrochloric Acid*

A small sample of the ester was heated under reflux with 0.225 *N* aqueous hydrochloric acid for 20 min. No obvious change occurred, and the concen-

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tration of hydrochloric acid was increased to 6 *N*. After three hours under reflux, the ester still floated as an oil on the surface; it was later recovered nearly quantitatively and with the correct melting point.

The xanthate ester, 0.300 gm., was then shaken with 25 ml. of ice-cold, concentrated hydrochloric acid (43.3%), but failed to react or dissolve within 24 hr. at 0°. The mixture was then diluted with an equal volume of water and extracted three times with ether to recover 0.308 gm. of a solid residue. Recrystallization from ethanol yielded 0.235 gm. (79%) of the pure *S*-methyl xanthate.

With cooling, 2 ml. of 12 *N* hydrochloric acid was diluted to 24 ml. with ethanol, and 15 ml. of the mixture was boiled under reflux for one hour with a small sample of the *S*-methyl xanthate. Although the latter dissolved, no odor of mercaptan was noticed. The mixture was evaporated, and after being filtered an ethereal extract of the residue yielded 97% of the starting material in a slightly impure state. Recrystallization gave the pure ester.

(*b*) *Methanolic Hydrogen Chloride (3.2%)*

O-Octadecyl *S*-methyl xanthate, 0.31 gm., was warmed under gentle reflux with 50 ml. of the acid reagent, an amount just sufficient to dissolve the ester. The top of the condenser was protected with a calcium chloride guard tube. After 30 min., a trace of methyl mercaptan could be detected by the yellow coloration imparted to lead acetate paper. This decomposition was exceedingly slow, because the product isolated after 72 hr. represented 93% of the original ester and had the correct melting point. The experiment was repeated using a sealed glass tube, which was kept at 120° for three days before being cooled and opened. The solution suddenly evolved much gas, which caused a mechanical loss of the product. The remaining product, 39%, was the original ester.

In another experiment, 0.2 gm. of the ester and 10 ml. of the methanolic hydrogen chloride were kept at 125° for three days, as before, but the tube and its colorless contents were further heated to 140° for two days, and then at 160° for 33 hr. Once more a violent evolution of gas destroyed the quantitative aspect of the recovery, but the product after recrystallization from pentane had the melting point, 59–60°, of octadecyl alcohol.

(*c*) *Acetic Anhydride – Zinc Chloride*

A small test tube containing the *S*-methyl xanthate, 0.5 gm., acetic anhydride, 2.5 gm., and anhydrous zinc chloride, 0.025 gm., was stoppered, shaken thoroughly, and kept at room temperature for 24 hr. When the mixture was poured onto ice, no solid appeared other than the original ester, which had never dissolved. Yield, 96.7%, with melting point correct at 37.5–38.5°.

Desulphurization of Octadecyl S-Methyl Xanthate

The pyrophoric Raney nickel "W-2" catalyst (19) was washed quite free of alkali and was stored under absolute ethanol. About 45 gm. of this catalyst, weighed wet with ethanol, was mixed with 7.2 gm. of octadecyl *S*-methyl

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xanthate and enough absolute ethanol to increase the volume to 150 ml. The mixture was boiled for four hours under reflux, and for at least an hour of this period a substance which turned lead acetate paper bright yellow and which had an unpleasant odor (not that of hydrogen sulphide) was evolved from the condenser. After being recovered by filtration through sintered glass, the residual nickel, still pyrophoric, was washed with warm ethanol, but still appeared to retain some of the product.

The filtrate and washings, from which a white solid tended to separate, were evaporated, and the residue was freed from traces of nickel by solution in ether and by filtration. After recovery from the ether the product, 5.4 gm., was fractionally recrystallized from pentane, absorbent carbon being used for clarification. The first two crops, totalling 2.2 gm. (40%), were shown by recrystallization to a melting point of 58–59° to be essentially octadecanol. Evaporation of the original mother liquors gave 1.97 gm. of a solid residue melting at 28.5–30°.

This residue when fractionated from methanol–ether yielded three crops of white ill-formed crystals; 0.742 gm., m.p. 28–30°; 0.333 gm., m.p. 28–30.5°; and 0.114 gm., m.p. 28–30.5°. The first fraction when recrystallized from methanol–ether melted at 29.5–31.5°. Found: OCH_3, 2.6, 2.6%. A combination of similar white, waxy residues from several experiments was then "recrystallized" twice from methanol without changing the melting point. Found: S (Carius), 2.1, 2.4, 2.3%. The product gave no green color with isatin in the test for a mercaptan (7), and did not dissolve in boiling 5% sodium hydroxide. A sodium hydroxide fusion test for oxidized sulphur (7), which depended on the change in color of nickelous hydroxide caused by sulphur dioxide, was no more positive than a blank. Although the substance was probably a mixture, it might have contained octadecyl methyl ether (calc. OCH_3, 10.9%).

In another experiment, in which 3.6 gm. of *O*-octadecyl *S*-methyl xanthate was treated with Raney nickel for only 10 min. near 10°, the low-melting residue from the crystallization of octadecanol weighed 1.35 gm. and melted at 27–28°. When fractionally recrystallized, the head fractions yielded 0.487 gm. of the original *S*-methyl xanthate with the correct melting point of 37°, which liberated mercaptan when heated with alcoholic sodium hydroxide.

Oxidations with Hydrogen Peroxide and Periodic Acid

(*a*) *O-Octadecyl S-Methyl Xanthate*

Seven grams (0.019 mole) of the xanthate ester was dissolved in 900 ml. of glacial acetic acid, an amount necessary to prevent precipitation of the ester when 11.3 ml. of 30% hydrogen peroxide (0.117 mole) was added with thorough mixing. About 90 min. later the clear solution began to deposit a white solid. After three days at room temperature, the liquor was diluted with an equal volume of water, the mixture was chilled, and the white, waxy precipitate isolated by a difficult filtration. Yield, 6.1 gm.; m.p., 49–52.5°. This product, when fractionally recrystallized, once from ethanol and twice from pentane, yielded 2.24 gm. (33.5%) of white flakes whose melting point

of 66–67° was not significantly changed by four more recrystallizations. Found: C, 58.6, 58.6; H, 10.1, 9.8; S, 15.5, 15.7, 15.6%; mol. wt. (Rast), 395, 420, 420, 426. Calc. for $C_{20}H_{40}O_4S_2$: C, 58.8; H, 9.9; S, 15.7%; mol. wt., 408.

The sodium hydroxide fusion test for oxidized sulphur (7) was no more positive than a blank, and another sample of the crystals was recovered with unchanged melting point after being boiled for 10 min. with concentrated hydrochloric acid. A third portion, when warmed briefly with 5% sodium hydroxide, melted, but resolidified to a white wax when the mixture cooled. In an attempt to saponify the compound, 1 gm. was heated under reflux with 30 ml. of 25% sodium hydroxide for seven hours, when no further change was apparent. The solid first melted, then partly solidified; finally the solution was yellow, and the substance floating on the surface had again liquefied. A steam distillation of the mixture produced a condensate containing a slightly volatile wax melting at 59.5–61.5°. This melting point, together with that of 79° found for the phenylurethane, identified the wax as octadecanol. The residue in the still gave a clear filtrate which liberated hydrogen sulphide when acidified and which produced a heavy black precipitate with a solution of lead acetate. Therefore at least one sulphur atom in the compound $C_{20}H_{40}O_4S_2$ was still in the reduced state. The acidified filtrate contained no sulphate ion, according to a test with barium chloride.

(*b*) *O-Hexadecyl S-Methyl Xanthate*

Following the procedure described for the octadecyl derivative, a solution of 13.3 gm. (0.04 mole) of the pure *O*-hexadecyl *S*-methyl xanthate in 1800 ml. of glacial acid was mixed with 0.24 mole of aqueous hydrogen peroxide. It was nearly a day before a precipitate began to form, and the product was isolated after three days. Yield, 8.5 gm. (56%); m.p., 42–44°. One recrystallization from ethanol and four from pentane raised this melting point to a constant value of 56–57°. Found: C, 57.0, 56.9; H, 9.6, 9.7; S (Waters), 17.0, 16.7%. Calc. for $C_{18}H_{36}O_4S_2$: C, 56.8; H, 9.5; S, 16.9%.

(*c*) *Paraperiodic Acid, H_5IO_6*

Octadecyl *S*-methyl xanthate was too insoluble to react with sodium periodate in water, and the reaction in 85% aqueous dioxane was very slow. In the final experiment, a solution of 1.9 gm. (8.3 mM.) of crystalline paraperiodic acid in 40 ml. of ethanol was mixed in a stoppered flask with 1 gm. (2.8 mM.) of the *S*-methyl ester in 100 ml. of ethanol. A deep red color soon developed in the solution, which after a week was diluted with 750 ml. of water. The silk-like precipitate containing iodine crystals was recovered, and the latter were allowed to evaporate in the open air. The remaining 0.339 gm. was recrystallized twice from ethanol–water to give a white wax melting at 33–34°.

Attempted Estimations of the Methylthio Group

(*a*) *With Hydriodic Acid*

The acid used boiled constantly at 127°, and good checks were obtained when the methoxyl content of vanillin (OCH_3, 20.4%) was determined both by the Kirpal–Bühn (13) and the Vieböck (23) methods.

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Found by the Vieböck method, with heating for 90 min.: SCH_3, 0.13, 1.15%; with heating for 150 min.: SCH_3, 0.51, 0.63%. Found by the Kirpal–Bühn method, with heating for five hours: SCH_3, 2.14, 2.42%. Calc. for *O*-octadecyl *S*-methyl xanthate, $C_{20}H_{40}OS_2$: SCH_3, 13.1%.

Found by the Vieböck method, with heating for one hour: SCH_3, 1.35, 2.34%. Found by the Kirpal-Bühn method, heating for four hours: SCH_3, 2.7, 1.9%. Calc. for benzyl *S*-methyl xanthate, $C_9H_{10}OS_2$: SCH_3, 23.7%.

(*b*) *With Bromine*

The method described by Siggia and Edsberg (22) for estimating thio ethers by oxidation to sulphoxides was modified. Weighed samples of pure *O*-octadecyl *S*-methyl xanthate were dissolved with difficulty in glacial acetic acid, a little hydrochloric acid was added, and the mixtures were titrated with 0.1 *N* potassium bromate – potassium bromide to a yellow end point. The end points were very indistinct, but corresponded roughly to the oxidation of both sulphur atoms in the xanthate ester. Attempts to keep the ester in solution by warming the acetic acid, or by replacing it with ethanol, gave still higher and still less reliable results. The ester reduced about 11 equivalents of bromine per mole.

In order to isolate the product, 8 gm. (0.022 mole) of the ester was dissolved in 600 ml. of warm ethanol and 50 ml. of water. This solution readily decolorized 7 ml. (about 13 equivalents) of bromine, a further 5 ml. being utilized within 16 hr. The orange liquid was then warmed to expel excess bromine and to redissolve a precipitate that had formed; 1.5 vol. of warm water was added, and a white wax, instead of an oil, separated provided that the solution cooled slowly to 10°. Yield, 6.3 gm. Three recrystallizations from pentane and two from ethanol rendered the melting point constant at 61.5–62.5°. This product gave negative tests for sulphur and halogens, did not dissolve in 5% sodium hydroxide, but turned bright yellow in color. A test for aldehyde group with dinitrophenylhydrazine was negative.

ACKNOWLEDGMENT

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THE CHEMISTRY OF LYCOCTONINE[1]

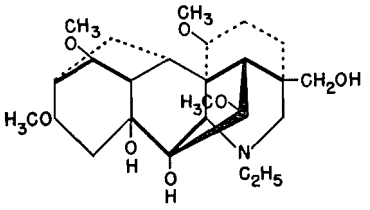
By O. E. Edwards, Léo Marion, and D. K. R. Stewart[2]

ABSTRACT

New observations in the chemistry of hydroxylycoctonine and other derivatives of lycoctonine, and the previously described reactions of the alkaloid, are interpreted using the structure as recently determined by X-ray crystallography.

During the last few years we have explored the chemistry of lycoctonine, and have proposed partial structures to account for the observed facts (3, 4, 5, 6). The determination in these laboratories of a total structure for des(oxymethylene)-lycoctonine using X-ray crystallography (11) makes it desirable to discuss these facts and further observations in the light of this formulation.

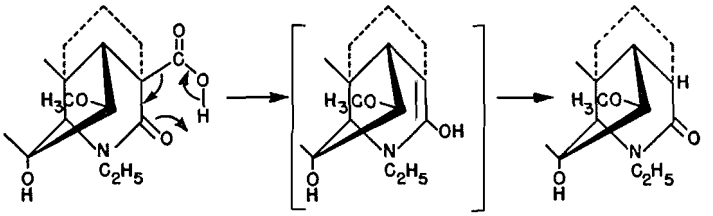
The proposed structure for des(oxymethylene)-lycoctonine leads without ambiguity to formula I or its mirror image for lycoctonine. The location of the



I

CH_2OH at the bridgehead of an azabicyclo[3,3,1]nonane system corresponds satisfactorily with the relatively unhindered nature of the carboxylic acid derived from it by oxidation of the primary hydroxyl and the methylene next to the nitrogen (lycoctonamic acid) (3). Roberts and Moreland (12) showed that esters of a similar acid in the bicyclo[2,2,2]octane series are readily hydrolyzed in contrast to acyclic tertiarily-bound carboxylic acids.

The transition state for the decarboxylation of lycoctonamic acid and the transient enolic intermediate would involve a bridgehead double bond as shown:



However, the work of Meerwein (9) has demonstrated that Bredt's rule can be violated to the extent of formation of such transient intermediates in the

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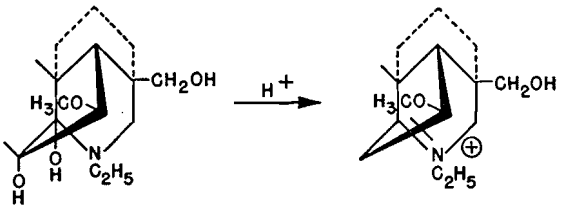
[2]*National Research Council Postdoctorate Fellow, 1955–56.*

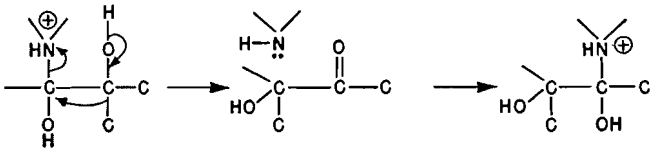
bicyclo[3,3,1]nonane system (see Reference 7 for an excellent review of Bredt's rule).

We have confirmed the observation of Cookson and Trevett (2) that hydroxylycoctonine (II) forms anhydronium salts (III). This is not too readily reconciled with the new structure, since the double bond demanded by this formation introduces marked strain.

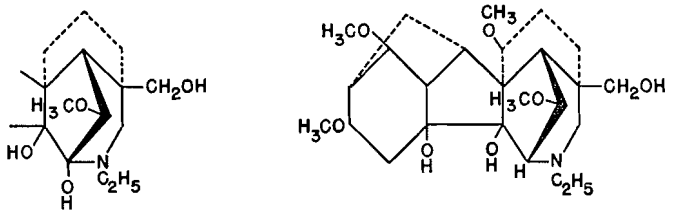


II III

If structure I is correct, then isolycoctonine, which is obtained by reduction of hydroxylycoctonine (II) in ethanolic-hydrochloric acid in the presence of Adams' catalyst (3), cannot be a simple epimer at the carbon next to the nitrogen as we had assumed. Hence it must be a rearrangement product. The simplest possibility seems to be that hydroxylycoctonine (II) is in equilibrium with the alternate masked α-ketol (IV) via the open ketone as shown:



If, now, IV is much more rapidly reducible than II as a result of the more exposed nature of the carbinolamine carbon, the production of V as the main product is understandable. We thus consider it probable that V is the structure of isolycoctonine. That the open ketone is present in acid solution is indicated



IV V

by the presence in ethanol solutions of hydroxylycoctonine salts and of hydroxylycoctonine in glacial acetic acid of a maximum at 320 mμ, ϵ 70. No such band is present in the solution of the anhydronium salts of atisine, isoatisine, and 17-hydroxylupanine.

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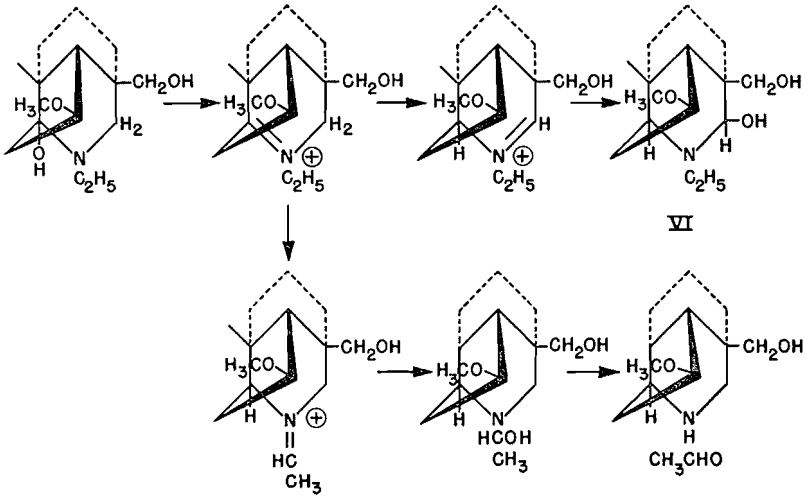
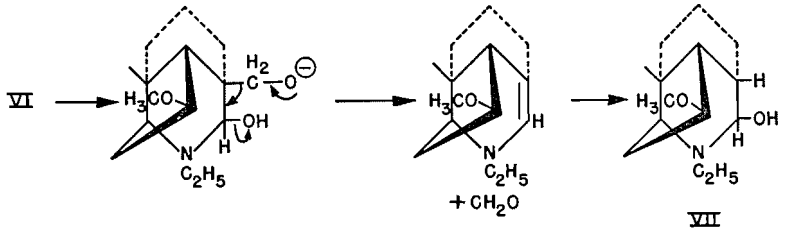
Hydroxylycoctonine was only slowly attacked by lithium aluminum hydride in refluxing dioxane. Sodium borohydride in aqueous alcohol gave a mixture of bases which was not further investigated.

The environment of the nitrogen readily accounts for the products obtained when an aqueous solution of hydroxylycoctonine was heated. The products identified were lycoctonine, des(oxymethylene)-lycoctonine, formaldehyde, and acetaldehyde. These can arise as shown using the partial formulae:



The carbinolamine VI can readily lose formaldehyde as shown:



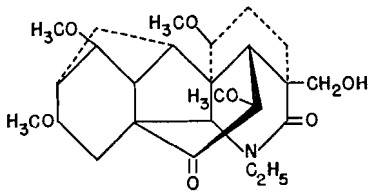
VI and VII are then reduced, presumably by the formaldehyde and some of the carbinolamine present, in crossed Cannizaro reactions to lycoctonine and des(oxymethylene)-lycoctonine respectively. A likely mechanism for reduction by formaldehyde is illustrated:

The facile loss of formaldehyde from VI provides an explanation of the formation of des(oxymethylene)-lycoctonam during permanganate oxidation

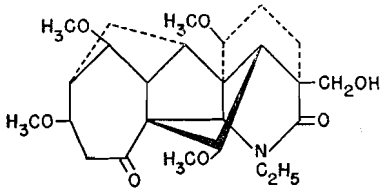
of lycoctonine. Thus VI must be formed as the first product of oxidation and have sufficient resistance to further oxidation that some has time to eliminate formaldehyde before the lactam is formed. That carbinolamines are intermediates in the permanganate oxidation of amines is also demonstrated by the formation of acetaldehyde from the N—C_2H_5 group of the aconite alkaloids (3).

It is evident that most of the chemistry of the heterocyclic ring is understandable on the basis of the new formula. However, one published fact which is in apparent conflict with the structure is the striking increase in resistance to hydrolysis of methyl hydroxylycoctonamate over methyl lycoctonamate (5), since the new hydroxyl and the carboxyl group are remote in space.

The geometry of the proposed structure demands that the pinacolic dehydration of the vicinal glycol in lycoctonam take one of two courses to give VIII or IX. Since IX should readily lose methanol to give an α-β unsaturated ketone with acid or base, it can be excluded from consideration since the anhydro compounds are relatively stable to these agents. Hence VIII must be the skeleton of anhydrolycoctonam (3, 6). The failure of anhydrolycoctonam



VIII



IX

to give readily a positive Fehlings and Tollens test was hence misleading as to the direction of the migration during the dehydration (6).

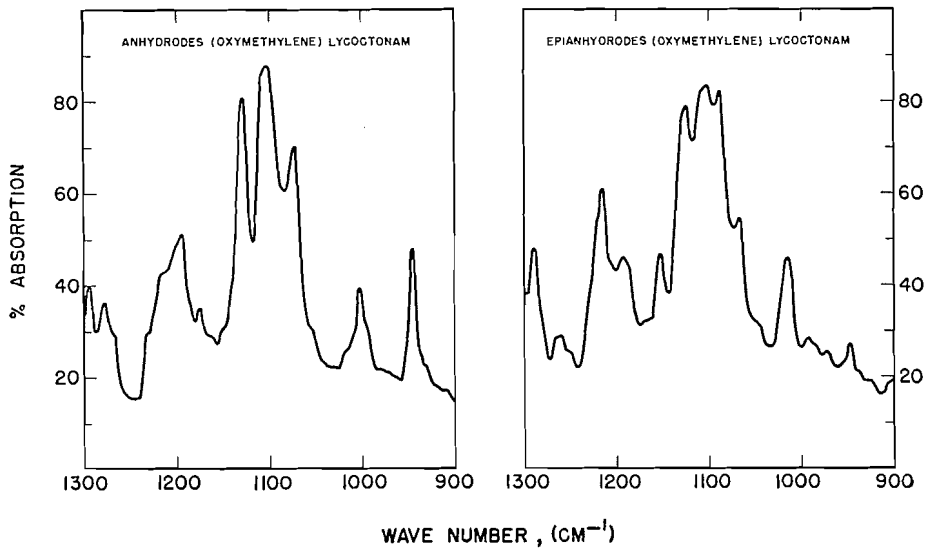


FIG. 1

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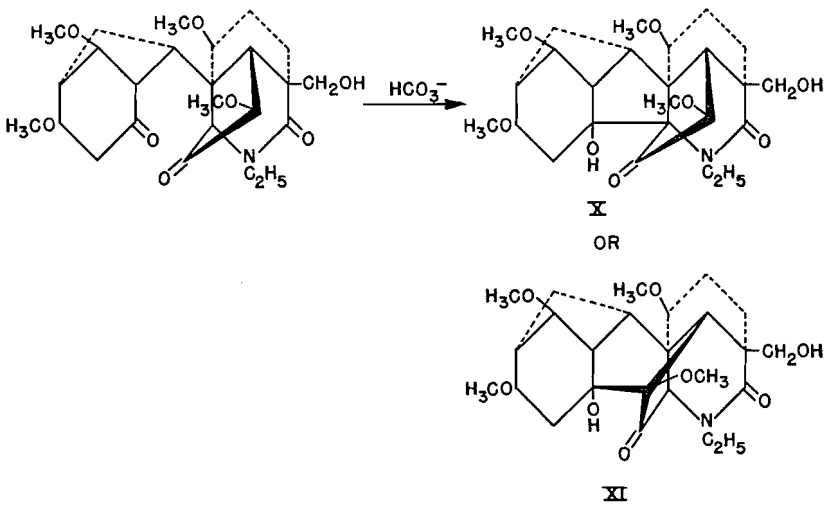
The interesting observation that, whereas anhydrolycoctonam (VIII) is stable to hot dilute alkali, anhydrodes(oxymethylene)-lycoctonam is transformed into an isomer is in harmony with the assigned structure. The reaction of anhydrodes(oxymethylene)-lycoctonam must be epimerization at the carbon α to the ketone carbonyl. This is borne out by the fact that the infrared spectrum of the product differs very little from that of the starting material, except for the disappearance of one methoxyl band at 1073 cm.$^{-1}$ and appearance of a new band at 1079 cm.$^{-1}$ (Fig. 1).

The replacement of the CH_2OH by hydrogen makes the epimer with the methoxyl directed toward this hydrogen the most stable one while the converse is true as long as the bulky CH_2OH is present (VIII).

Most of the reactions of the secodiketones derived by periodate cleavage of the vicinal glycol are readily accounted for using the new formula. The "iso" compounds derived from the secodiketones by adsorption on weakly acidic alumina or by treatment with sodium bicarbonate (4) must be the internal aldol condensation product XI:

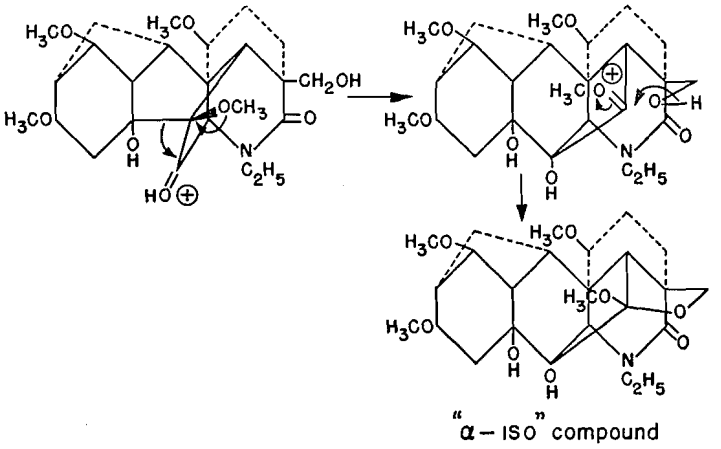


X

XI

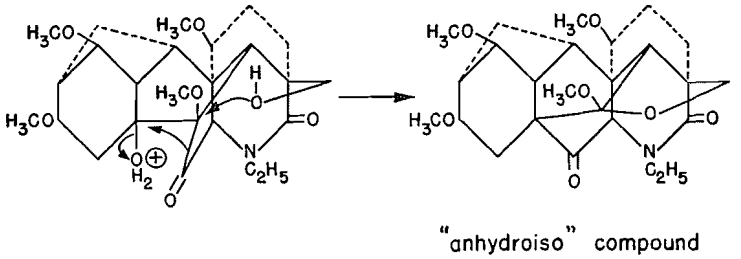
The methoxyl at the point of condensation may be epimerized during the preparation of the secodiketones, or during the condensation, to give XI. The structure X is unlikely since the enolization of the ketone in the requisite direction for its formation would place a bridgehead double bond in the small branch of an azabicyclo[3,2,1]octane system in serious violation of Bredt's rule.

The action of hot dilute acid on the "iso" compound gave rise to a mixture from which two crystalline products (called the "α-iso" and "anhydroiso" compounds) were obtained (4). The "α-iso" compound, which was isomeric with the "iso" compound, but had lost the ketonic function and the primary hydroxyl while gaining a new hindered hydroxyl, we consider to arise from XI as shown:



It is intriguing that in this structure the lycoctonine skeleton, including the vicinal glycol, has been re-formed. Experiments are underway to test this hypothesis.

The "anhydroiso" compound, which from analyses and spectra seemed to be the product of ether formation between the primary and tertiary hydroxyl, can be explained by postulating an acyl migration (probably a two step process as for the "α-iso" compound):



House and Reif (8) and Meinwald (10) have discussed similar migrations. The geometry is good for the migration, and the final structure, while somewhat crowded, is not particularly strained. The position of the carbonyl absorption in the infrared for the "anhydroiso" compound (1736 cm.$^{-1}$) is high for the suggested six-membered character. (The somewhat comparable carbonyl in the anhydrolycoctonam types, however, absorbs as high as 1740 cm.$^{-1}$.)

The survival of the ketals in the hot acid, if the above postulates are correct, calls for comment. The double bond in the oxonium ion intermediate in the most probable hydrolysis pathway does not appear unduly strained in models. However, the moderate strain in this intermediate, the competitive protonation of the ring oxygen (which probably would not lead to hydrolysis), and protonation of the more basic lactam may all combine to make hydrolysis of the ketal a slow process.

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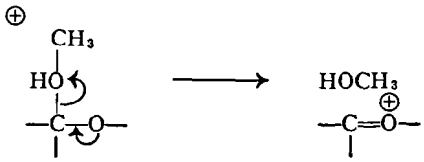

The failure of hydroxylycoctonine to consume more than 1 mole of HIO_4 led us to the conclusion that there was no vicinal triol system in the compound. Since the new formula demands the presence of such a triol, the cleavage was tested further. Hydroxylycoctonine reacts with 1 mole of $Pb(OAc)_4$ in 48 hr. in dilute acetic acid solution, but the reagent is taken up steadily beyond this until after 528 hr. 3.5 moles have been consumed. Hydroxylycoctonam on the other hand rapidly takes up 1 mole of $Pb(OAc)_4$ but the oxidation then stops. After 315 hr. only 1.26 moles is taken up, no more than is consumed by lycoctonam itself. That the oxidation cleaves the original vicinal glycol is demonstrated by the infrared spectrum of the resulting diketone which has carbonyl bands at the same frequency as *seco*lycoctonam diketone, and the formation of a desmethanol derivative during the oxidation or subsequent chromatography with infrared and ultraviolet spectra again very similar to desmethanol-*seco*lycoctonam diketone. Hydroxy*seco*lycoctonam diketone monoacetate is resistant to permanganate oxidation in acetone, and inert to sodium bismuthate in acetic acid at room temperature. Only a small quantity of acidic material was produced when desmethanolhydroxy*seco*-lycoctonam diketone was treated at 0° with alkaline hydrogen peroxide. Thus we have been unable to provide direct evidence for the presence of a vicinal triol in hydroxylycoctonam.

A third neutral compound which was strongly adsorbed on alumina was isolated from among the lead tetraacetate cleavage products. It appears to have the empirical formula $C_{24}H_{35}NO_9$. Since it was not readily acetylated it probably has no primary hydroxyl while the spectra indicate the presence of two ketone carbonyls, at least one hydroxyl, and the lactam. The properties are consistent with a structure in which the CH_2OH of the *seco* diketone has been replaced by OH.

The work reported in this paper clearly shows the difficulty of demonstrating two of the vital points needed in determining the structure of lycoctonine by chemical means: whether or not hydroxylycoctonine has the same skeleton as lycoctonine, and the relation between the heterocyclic ring and vicinal glycol. The difficulties encountered in attempts to determine the degree of substitution of the carbon holding the hydroxymethylene group will be described in a later paper. Thus it appears that the solution of the structural problem by ordinary degradative methods would have been extremely difficult.

Finally, it must be pointed out that the suggestions advanced in an earlier paper (6) for the course of the acid-catalyzed transformation of anhydrolycoctonam into lycoctamone are untenable and the structure of lycoctamone is as yet unsettled. One possible formulation of this interesting product is currently being tested experimentally.

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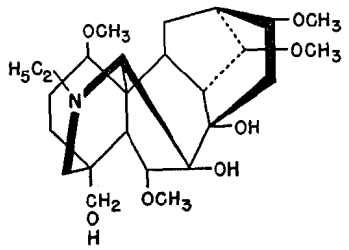
While the chemistry of delpheline (1) is readily interpreted using the same carbon skeleton as that of lycoctonine, the reactions of delphinine, in particular the two-stage Hofmann degradation (13) and the Grignard reactions of oxodelphinine (14), seem to demand a different sort of structure for this alkaloid.

The structure of lycoctonine can be projected in such a way as to emphasize its diterpenoid character*:



Since atisine, the only other aconite alkaloid about which much is known, almost certainly has a diterpenoid carbon skeleton also, it seems likely that all delphinium and aconite alkaloids will be found to have structures derived from various modified diterpenoid skeletons.

EXPERIMENTAL

Rotations were determined in absolute ethanol, the cited temperature being that of the room. The ultraviolet spectra were determined on solutions in 95% ethanol using a Beckmann D.U. spectrophotometer. Infrared spectra were determined on a Perkin-Elmer model 21 double beam spectrophotometer.

Hydroxylycoctonine

When prepared by oxidation of lycoctonine with a mole of $Pb(OAc)_4$ in acetic acid (2) the compound was obtained in 75% yield. It readily crystallized from concentrated acetone solution as rectangular plates. Its physical constants were very close to those described earlier (3): m.p. 148–152°, $[\alpha]_D$ $+13°\pm1°$ (*c*, 2.0 in ethanol). Its infrared spectrum (nujol mull) had no bands between 1500 and 2800 $cm.^{-1}$.

The hydriodide of the base, m.p. 198° dec., when reanalyzed gave figures in good agreement with theory for an anhydronium salt. Found: C, 50.51, 50.94; H, 6.70, 6.82. Calc. for $C_{25}H_{42}NIO_7$: C, 50.58; H, 6.79. The infrared spectrum of the salt (nujol mull) contained bands at 1670 and 1712 $cm.^{-1}$ as described by Cookson and Trevett (2). The relative intensity of these bands was unaffected by the mode of preparation of the salt, or by heating it dry or in methanol solution. Its ultraviolet absorption spectrum had strong featureless absorption at short wavelengths (log ϵ 3.39 at 240 mμ and 3.04 at 250 mμ) and λ_{min} 305 mμ (log ϵ 1.72), λ_{max} 330 mμ (log ϵ 1.85). The absorption spectrum of a solution of hydroxylycoctonine in acetic acid had λ_{max} 330 mμ (log ϵ 1.85).

**We are indebted to Dr. R. C. Cookson who pointed out this fact in a private communication.*

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Reduction of Hydroxylycoctonine

Approximately 350 mgm. of lithium aluminum hydride in 25 ml. of ether was added to a solution of 300 mgm. of hydroxylycoctonine in 15 ml. of dioxane. The ether was boiled off and the dioxane solution refluxed under nitrogen for two hours. The excess reagent was decomposed with ethyl acetate, the dioxane removed *in vacuo*, 15 ml. of saturated Rochelle salt solution added, and the base extracted into methylene chloride. The extract gave 280 mgm. of methanol-soluble base. This crystallized from concentrated aqueous methanol, giving 170 mgm., m.p. 149–152°, which did not depress the melting point of hydroxylycoctonine. The remaining base would not crystallize.

A solution of 100 mgm. of hydroxylycoctonine in 2 cc. of 50% aqueous methanol containing 89 mgm. of sodium borohydride was left at room temperature for 18 hr. A concentrated aqueous solution of the 83 mgm. of base recovered from the reaction deposited 20 mgm. of crystals, m.p. 156–161°. The mother liquors were acidified, warmed for five minutes, then left at room temperature for two hours. The 65 mgm. of base recovered from this solution slowly crystallized from water on addition of ammonia, giving 32 mgm. of tiny plates, m.p. 128–134°. When recrystallized from acetone this gave rectangular plates, m.p. 132–140°. Mixed m.p. with hydroxylycoctonine 137–145°. The base in the mother liquors remained amorphous.

Action of $Pb(OAc)_4$ on Hydroxylycoctonine

A solution was prepared of 76 mgm. of hydroxylycoctonine in 15 cc. of a 0.056 molar solution of lead tetraacetate in acetic acid. At intervals an aliquot was removed, added to a solution of potassium iodide in saturated sodium acetate containing a known excess of sodium thiosulphate solution, and the excess back-titrated with iodine. The mole ratio of lead tetraacetate consumed was 0.60 (24 hr.); 1.08 (48 hr.); 1.79 (96 hr.); 2.35 (166 hr.); 2.74 (239 hr.); 3.22 (382 hr.); 3.5 (528 hr.).

Action of Hot Alkali on Hydroxylycoctonine

A solution of 40 mgm. of hydroxylycoctonine in 5 cc. of methanol containing 240 mgm. of potassium hydroxide was refluxed for six hours, then left overnight at room temperature. The recovered base (40 mgm.) gave 18 mgm. of starting material, m.p. 148° (mixed m.p. 149°). The residual base or its hydriodide could not be obtained crystalline. This residue had $[\alpha]_D$ −12° (*c*, 1.6 in ethanol), hence a new base or bases had been formed.

Heating of Hydroxylycoctonine in Water and Aqueous Alcohol

(*a*) 333 mgm. of pure hydroxylycoctonine in 6 cc. of 20% ethanol in water was heated at full steam bath temperature for eight hours, then left overnight at room temperature. The solution was taken to near dryness under reduced pressure. The residue when diluted with water deposited 135 mgm. of fine needles, m.p. 110–115°, $[\alpha]_D$ +44° (*c*, 1.88 in EtOH), which when mixed with lycoctonine melted at 117–130° dec. The mother liquor was acidified and extracted with methylene chloride, the organic phase yielding 8 mgm. of

amorphous neutral material. The acid solution on basification and extraction with methylene chloride gave 150 mgm. of amorphous base with $[\alpha]_D$ +41° (*c*, 3.0 in ethanol).

The amorphous base was combined with 28 mgm. of similar base from a previous run, and converted to its hydriodide. A solution of this deposited 29 mgm. of hydriodide, m.p. 194° dec. (infrared spectrum identical with that of lycoctonine hydriodide). The mother liquor on addition of ether gave 88 mgm. of crystals, m.p. 150° dec., which proved to be impure des(oxymethylene)-lycoctonine hydriodide (see below).

Formaldehyde Characterization

(*b*) Hydroxylycoctonine (55 mgm.), 45 mgm. of dimedon, and 34 mgm. of anhydrous sodium carbonate in 3 cc. of water gave a clear solution when heated, which had a pH near eight. This was heated on the steam bath under a condenser for four hours. The solution was cooled and neutralized with dilute sulphuric acid. The 21 mgm. of precipitate that formed, when recrystallized from methanol, separated as needles, m.p. 192–193°. A mixture with authentic dimedon–formaldehyde derivative (193–194°) melted at 192–193.5°.

(*c*) A solution of 151 mgm. of hydroxylycoctonine in 5 cc. water was heated for four hours on the steam bath, cooled, and the solution filtered. Forty-one milligrams of lycoctonine, m.p. 118–126°, was obtained. A few drops of the filtrate was added to 5 cc. of chromotropic acid in 50% sulphuric acid. A purple color appeared after a few minutes' heating at 100°, and increased steadily in intensity. The solution after 0.5 hr. had the intense maximum ($E_{1\ cm.}$ = 1.05) at 570 mμ characteristic of the condensation product with formaldehyde. Hydroxylycoctonine alone (2 mgm. in 8 ml. of reagent) slowly developed a purple color at 100°, which after 0.5 hr. was still weak ($E_{1\ cm.}$ = 0.12).

Acetaldehyde

(*d*) 244 mgm. of hydroxylycoctonine and 76 mgm. of anhydrous sodium carbonate in 7 cc. of water was heated on the steam bath for 3.5 hr. while nitrogen was bubbled through. The nitrogen was passed through a solution of *p*-nitrophenylhydrazine in dilute acetic acid. After 0.5 hr. a crystalline hydrazone began to separate. At the end of the reaction period 11 mgm. of a *p*-nitrophenylhydrazone had formed, m.p. 124–128°. After two recrystallizations from aqueous methanol the derivative was obtained as fine needles, m.p. 125–129°. Its mixed melting point with acetaldehyde *p*-nitrophenylhydrazone (129–131°) was 126–129°. The main reaction mixture deposited 41 mgm. of needles, m.p. 115–120°. After one recrystallization this melted at 120–127° and did not depress the melting point of lycoctonine. The aqueous mother liquor contained 66 mgm. of neutral product and 94 mgm. of bases. The latter when converted to hydriodide gave 32 mgm. of lycoctonine hydriodide, m.p. 193° dec. (infrared comparison).

Des(oxymethylene)-lycoctonine

Approximately 140 mgm. of the more soluble non-crystalline products from runs similar to (*c*) when separated gave 125 mgm. of bases and 11 mgm. of

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neutral products. The bases were converted to hydriodide and crystallized from acetone. A first crop of 20 mgm. of lycoctonine hydriodide was followed by two crops totaling 89 mgm. melting at 175° (dec.). After two recrystallizations this salt melted at 176–177° dec. It did not depress the melting point of des(oxymethylene)–lycoctonine hydriodide monohydrate and the infrared spectra of the two were identical.

Epimerization of Anhydrodes(oxymethylene)-lycoctonam

(*a*) A solution of 35 mgm. of anhydrodes(oxymethylene)-lycoctonam (3) in 5 cc. of 50% aqueous methanol containing 160 mgm. of potassium hydroxide was refluxed for three hours. The 34 mgm. of neutral product crystallized nearly quantitatively as short stout needles from ether. After two recrystallizations 15 mgm. was obtained, m.p. 148–151°, $[\alpha]_D$ +18°±2° (*c*, 0.60). Its infrared spectrum was similar to that of the starting material but contained bands attributable to the epimer.

(*b*) A solution of 116 mgm. of anhydrodes(oxymethylene)-lycoctonam ($[\alpha]_D^{23}$ −8°±1° (*c*, 1.8)) in a mixture of 2 cc. of methanol and 3 cc. of water containing 300 mgm. of potassium hydroxide was refluxed for six hours. The clear yellow solution was concentrated to half volume under reduced pressure, then the product extracted into methylene chloride. The 115 mgm. of pale pink froth crystallized readily from solution in ether. Crop 1, 57 mgm., m.p. 175–190° (hot stage). Crop 2, m.p. 165–175°. Crop 1 when recrystallized from acetone–ether gave a first crop of rhombic plates, m.p. 180–185°, $[\alpha]_D^{23}$ +27° (*c*, 1.95).

Several similar lots of high melting material were recrystallized twice from ethyl acetate – ether, giving prisms showing faint signs of melting at 180° and completely melted by 190° (hot stage), $[\alpha]_D^{22}$ +33° (*c*, 1.45). Its infrared spectrum (mull) had a carbonyl band at 1740 cm.$^{-1}$. Part of the "fingerprint" region is shown in Fig. 1. Found: C, 66.30; H, 8.26; OCH_3, 28.58. Calc. for $C_{24}H_{35}O_6N$: C, 66.50; H, 8.14; $4OCH_3$, 28.63.

Oxidation of Lycoctonam

A 1.00×10^{-2} molar solution of lycoctonam in a saturated solution of lead tetraacetate in glacial acetic acid consumed 1.02 moles of reagent in 2 hr., 1.11 moles in 50 hr., and 1.44 moles in 187 hr.

Oxidation of Hydroxylycoctonam

Hydroxylycoctonam, m.p. 205–208°, (Found: C, 60.16; H, 7.75. Calc. for $C_{25}H_{39}NO_9$: C, 60.34; H, 7.90) (5), was dissolved in a saturated solution of lead tetraacetate to give a 1.00×10^{-2} molar solution. The compound consumed the following mole ratios of reagent: 0.94 (2 hr.), 0.98 (5 hr.), 1.05 (26 hr.), 1.18 (119 hr.), 1.26 (315 hr.). The rate of oxidation did not change when the solvent was 5% and 30% water in acetic acid.

A solution of 3.07 gm. of hydroxylycoctonam in 600 ml. of a saturated solution of lead tetraacetate in acetic acid was left for two hours at room temperature. Saturated sodium sulphite solution was added to reduce excess reagent and the solvent removed under reduced pressure. The residue was taken up in water and the lead salts removed by filtration. The filtrate was

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acidified with dilute sulphuric acid and extracted with methylene chloride. The methylene chloride after washing with sodium bicarbonate solution yielded 2.39 gm. of white foam.

The product was adsorbed from benzene onto 96 gm. of neutral alumina, activity 4. A summary of the chromatogram follows:

Eluant	Weight eluted, mgm.
(*a*) Benzene (300 cc.)	125
(*b*) 25% chloroform in benzene (900 cc.)	2124
(*c*) 1% methanol in chloroform (200 cc.)	532
(*d*) 1% methanol in chloroform (100 cc.)	334
(*e*) 50% methanol in chloroform (100 cc.)	128

None of the fractions would crystallize, hence they were acetylated at room temperature with acetic anhydride – pyridine. Group (*a*) yielded 40 mgm. of pure des(oxymethylene)hydroxy*seco*lycoctonam diketone monoacetate and some less pure material. Group (*b*) gave first crops totaling 919 mgm., mainly hydroxy*seco*lycoctonam diketone monoacetate. The first fractions, however, appeared contaminated with the des(oxymethylene) compound ($[\alpha]_D$ −42°) and the last fractions with the strongly adsorbed third compound ($[\alpha]_D$ −38°). From fractions (*d*) and (*e*) was obtained 278 mgm. of the third compound.

Hydroxysecolycoctonam Diketone Monoacetate

The compound crystallized from acetone on addition of ether, m.p. 203–206°, $[\alpha]_D$ −33° (*c*, 1.25). Found: C, 60.45; H, 7.21; OCH_3, 23.16; acetyl, 8.15. Calc. for $C_{27}H_{39}NO_{10}$: C, 60.32; H, 7.31; $4OCH_3$, 23.1; acetyl, 7.81. Its ultraviolet spectrum had a shoulder centering around 280 mμ (log ε 1.91); log ε at 220 mμ was 3.16.

Infrared spectrum (51 mgm. 1 ml. in chloroform, 0.1 mm. cell): 3010(39), 2960(38), 2840(25), 1750(83), 1710(57), 1666(72), 1465(38), 1375(49), 1210–40(74), 1100(77), 1047(58), 990(41), 955(43).

Sodium Bismuthate on the seco Diketone

Hydroxy*seco*lycoctonam diketone acetate (59 mgm.) was dissolved in 5 ml. of acetic acid. Several milligrams of sodium bismuthate was added. No reduction of the bismuthate was evident after three hours at room temperature. After addition of the balance of 1 molar equivalent of $NaBiO_3$ (31 mgm.) the mixture was left for 16 hr. No apparent oxidation of the compound had taken place, hence the reaction mixture was heated at 80°. In 20 min. the color of the Bi_2O_5 was gone. The acetic acid was removed under reduced pressure and the residue extracted with acetone. The material left on evaporation of the acetone was dissolved in methylene chloride and the solution washed with sodium bicarbonate solution. The methylene chloride contained 54 mgm. of neutral material which crystallized from acetone on addition of ether giving 16 mgm., m.p. 182–190°. The infrared spectrum of this proved

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identical with that of desmethanolhydroxy*seco*lycoctonam diketone monoacetate. A further 14 mgm. of cruder material, m.p. 180–186°, was obtained from the mother liquor.

Desmethanolhydroxysecolycoctonam Diketone Monoacetate

The compound when crystallized from acetone–ether had m.p. 192–195°, $[\alpha]_D^{22}$ −47° (*c*, 1.50). Found: C, 61.94; H, 6.93; OCH_3, 18.31; acetyl, 8.64. Calc. for $C_{26}H_{35}NO_9$: C, 61.77; H, 6.98; $4OCH_3$, 18.4; acetyl, 8.31. Ultraviolet spectrum: λ_{max} 230–233 mμ (log ε 3.74); λ_{min} 280 mμ (log ε 1.40); λ_{max} 315 mμ (log ε 1.64). Infrared spectrum (61 mgm. 1 ml. in chloroform, 0.1 mm. cell): 3010(42), 2960(43), 2840(23), 1750(90), 1665(84), 1465(46), 1375(54), 1210–40(80), 1110(81), 1050(66), 985(44), 955(49), 910(22), 830(25).

Alkaline Hydrogen Peroxide on the Desmethanol Diketone

Desmethanolhydroxy*seco*lycoctonam diketone acetate (100 mgm.) was dissolved in 5 cc. of methanol and the solution cooled to 0°. A solution of 150 mgm. of potassium hydroxide in 1 cc. of methanol was added, followed by 1 cc. of 30% hydrogen peroxide and 3 cc. of methanol to clarify the solution. This was stirred at 0° for 10 min., diluted with water and extracted with methylene chloride, then acidified and extracted again with methylene chloride. The combined extracts were separated into 92 mgm. of neutral and 6 mgm. of acidic material. Neither product was obtained crystalline.

Strongly Adsorbed Ketone

When crystallized from acetone–ether this melted at 209–213°, $[\alpha]_D^{23}$ −110° (*c*, 2.67). Found: C, 60.15; H, 7.27; OCH_3, 23.2. Calc. for $C_{24}H_{35}O_9N$: C, 59.86; H, 7.33; $4OCH_3$, 25.8.

Ultraviolet spectrum: Shoulders around 230 mμ (log ε 3.0) and 275 mμ (log ε 1.8).

Infrared spectrum (60 mgm. 1 ml. in chloroform, 0.1 mm. cell): 3440(28), 3010(52), 2960(50), 2900(33), 2840(31), 1757(76), 1715(68), 1650(83), 1485(47), 1470(54), 1420(32), 1385(29), 1360(25), 1330(30), 1290(48), 1205–1240(51), 1175(42), 1110(87), 1060(75), 980(47), 910(21).

The compound was recovered unchanged after 16 hr. in acetic anhydride – pyridine (1:1) solution.

ACKNOWLEDGMENT

We are indebted to Dr. R. C. Cookson and Dr. M. Trevett for informing us prior to publication of their observations on hydroxylycoctonine and to Dr. Cookson for his comments on the diterpenoid nature of lycoctonine. We wish to thank Dr. R. N. Jones and Mr. R. Lauzon for obtaining the infrared spectra, and Mr. H. Seguin for the analyses.

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DÉRIVÉS DU TRIMÉTHYL-1,8,8 BICYCLO[3,2,1]OCTANE

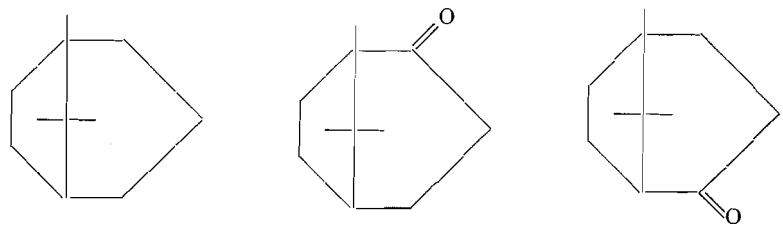
I. LA RÉACTION DU DIAZOMÉTHANE AVEC LA CAMPHOQUINONE[1]

PAR H. FAVRE, B. MARINIER[2] ET J-C. RICHER[2]

RÉSUMÉ

On montre dans ce mémoire que le diazométhane réagit avec la camphoquinone pour donner un mélange de méthoxy-4 triméthyl-1,8,8 bicyclo[3,2,1]octène-3 one-2 et de méthoxy-4 triméthyl-5,8,8 bicyclo[3,2,1]octène-3 one-2. Ces éthers cétoénoliques de la triméthyl-1,8,8 bicyclo[3,2,1]octanedione-2,4 ont été séparés, leur bromation et leur oximation étudiées, leur dégradation effectuée par réduction par l'hydrure de lithium et d'aluminium suivie d'un traitement acide; on a obtenu respectivement la triméthyl-5,8,8 bicyclo[3,2,1]octène-3 one-2 et la triméthyl-1,8,8 bicyclo[3,2,1]octène-3 one-2, dont l'hydrogénation de la liaison éthylénique conduit à l'homoépicamphre et à l'homocamphre.

Des difficultés de synthèse ont rendu peu accessibles les dérivés du triméthyl-1,8,8 bicyclo[3,2,1]octane (I), homologue supérieur du bornane. Il nous a paru utile d'entreprendre dans ce domaine une étude systématique et comparée des cétones, des alcools et des amines, dont la fonction se situe sur le chaînon tricarboné. Seules quelques cétones sont connues : l'homocamphre (II) (4, 5, 9), l'homoépicamphre (III) (12) et la triméthyl-1,8,8 bicyclo[3,2,1]octanedione-2,4 (IV)[3] (3, 6, 8, 9). Notre premier objectif fut la synthèse des monocétones II et III.



I II III

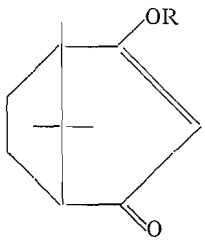
Nous nous sommes inspirés d'un travail de Rupe et Frey (9)[4]; ces auteurs ont préparé l'homocamphre (II) à partir de la camphoquinone par l'intermédiaire de la dictétone IV. Nous avons décidé de mettre en oeuvre cette dicé-

[1]*Manuscrit reçu le 18 mai, 1956.*
Contribution du Département de Chimie de l'Université de Montréal, Montréal, P.Q. Ce mémoire a été présenté au 14e Congrès International de Chimie pure et appliquée, Zurich, 21–27 juillet, 1955; il est tiré, en partie, des mémoires de maîtrise de B. Marinier et J-C. Richer.
[2]*Boursier du Conseil National de Recherches du Canada.*
[3]*Le symbole IV représente l'ensemble des trois structures distinctes IVa (forme dicétonique), IVb et IVc (formes céto-énoliques).*
[4]*Nous avons écarté d'emblée, en raison de leur faible rendement global, les synthèses qui font appel à un procédé de cyclisation pour la formation du noyau bicyclo[3,2,1]octanique, tant pour la synthèse de l'homocamphre (4, 5, 9) et de l'homoépicamphre (12) que pour celle de la dicétone IV (3, 6, 8). Rupe et ses collaborateurs (9, 10) ont montré que l'on pouvait passer d'un seul jet et avec un rendement excellent du noyau bicyclo[2,2,1]heptanique au noyau bicyclo[3,2,1]octanique par un procédé d'extension de cycle.*

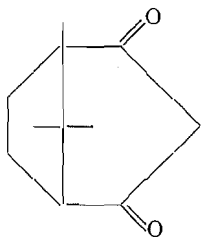
tone IV et d'en tirer deux monocétones, à l'image de la production des cétones $\alpha\beta$-éthyléniques à partir des éthers céto-énoliques des dicétones β alicycliques (1, 2), selon le schéma suivant :

$$-C(OCH_3)=CH-CO- \xrightarrow{LiAlH_4} -C(OCH_3)=CH-CHOH- \xrightarrow{H^+} -CO-CH=CH-.$$

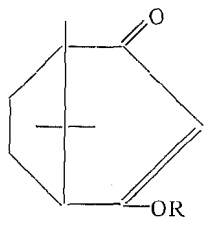
La méthode de Rupe et Frey (9) semblait être particulièrement bien adaptée à notre projet, puisque ces auteurs ont montré que l'action du diazométhane sur la camphoquinone conduit à un mélange des deux éthers céto-énoliques méthyliques de la dicétone IV. Un doute cependant planait sur la structure de ces éthers. D'une part, Rupe et Frey (9) leur assignèrent les structures V*d* et V*c* (correspondant respectivement à un éther solide p.f. 54–55°, $[\alpha]_D^{20} = -29.3°$,[5] de structure soit-disant *trans*, et à un éther liquide, $[\alpha]_D^{20} = +1.1°$, de structure *cis*). Isshiki (3) proposa d'autre part, sans toutefois apporter de preuves à l'appui, les structures V*b* et V*c*, prévues par la théorie pour une dicétone β asymétrique.



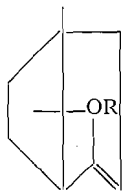
IV*b* R = H
V*b* R = CH_3



IV*a*



IV*c* R = H
V*c* R = CH_3



IV*d* R = H
V*d* R = CH_3

Ces divergences nous ont conduits à reprendre l'étude de l'action du diazométhane sur la camphoquinone. Nous avons trouvé que le mélange brut issu de la réaction se sépare bien, comme l'ont montré Rupe et Häfliger (10) puis Rupe et Frey (9), en un solide p.f. 56°, $[\alpha]_D^{23} = -29.0°$, et un liquide, $[\alpha]_D^{23} = -3.9°$. En soumettant ce liquide à une distillation fractionnée, il est possible d'en retirer, par cristallisation des fractions, deux composés solides : l'un est l'éther p.f. 56°, déjà décrit, l'autre est un éther isomère p.f. 71°, $[\alpha]_D^{23} = +33.9°$.Le mélange de ces deux éthers céto-énoliques constitue 88.5% du mélange brut et le rapport des pourcentages des éthers p.f. 56° (V*c*) et p.f. 71° (V*b*) est d'environ (65–68)/(35–32). Les deux éthers solides sont facilement hydrolysés par l'acide chlorhydrique, à température ambiante, en dicétone IV ; ils se forment tous deux lorsque cette dicétone β réagit avec un excès de diazométhane.

Pour déterminer les positions respectives du carbonyle et du méthoxyle dans les deux isomères p.f. 56° et p.f. 71°, nous avons mis en oeuvre la méthode d'élimination du carbonyle mentionnée plus haut, en appliquant le mode opératoire de Seifert et Schinz (13).

L'isomère p.f. 71° conduit à un mélange complexe, duquel on retire par chromatographie sur alumine 50% environ de triméthyl-1,8,8 bicyclo[3,2,1]oc-

[5]*Toutes les valeurs du pouvoir rotatoire données dans ce mémoire s'entendent pour des solutions benzéniques, sauf indication contraire.*

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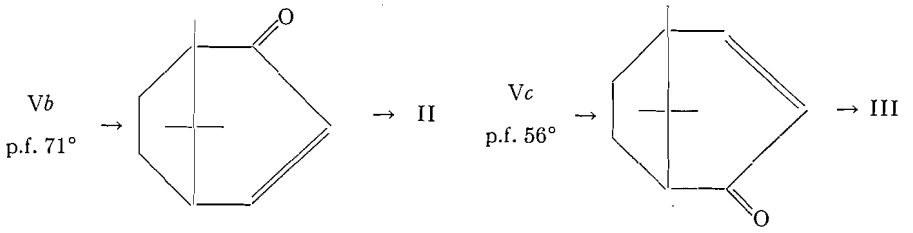
tène-3 one-2 (VI), dont le point de fusion (174–176°) et le pouvoir rotatoire (−55.3°) sont en bon accord avec les valeurs données par Rupe et Frey (9). La marche de la purification fut suivie par l'analyse de l'absorption dans l'ultraviolet dans la région de 230 mμ et par hydrogénation catalytique de la liaison éthylénique. L'hydrogénation d'échantillons très purs conduit à l'homocamphre (II) p.f. 187–190°, $[\alpha]_D^{23} = -108.9°$, identique à un homocamphre que nous avons préparé selon les indications de Lapworth et Royle (4). L'identité des deux cétones fut démontrée par absorption infrarouge. Le test du point de fusion de mélange, bien que positif, a peu de valeur; en effet les cétones II et III, ainsi que VI et VII, ne donnent pas de dépression de point de fusion lorsqu'elles sont mélangées entre elles dans les conditions habituelles du test; l'interprétation des points de fusion et des points de fusion de mélange est ainsi rendue très difficile (voir à ce sujet Pirsch (7)). Le pouvoir rotatoire est le meilleur critérium de pureté; il est légitime d'admettre que l'homocamphre de Lapworth et Royle (4), en raison de sa méthode de préparation, est un composé pur et exempt d'isomères et par suite de prendre son pouvoir rotatoire comme standard.

On n'arrive à l'homocamphre pur, par dégradation de l'éther céto-énolique p.f. 71°, qu'en effectuant une purification soignée au niveau de la cétone non saturée VI; la purification—par chromatographie sur alumine, sublimation fractionnée ou passage par la semicarbazone—mise en oeuvre sur des échantillons d'homocamphre issu de la cétone VI brute ou insuffisamment purifiée ne convient pas. Le passage par le semicarbazone a toutefois permis de mettre en évidence une cétone isomère de l'homocamphre, à pouvoir rotatoire fortement lévogyre; nous n'avons pas pu l'isoler à l'état de pureté.



VI VII

L'isomère p.f. 56°, à son tour, donne naissance à une cétone αβ-éthylénique p.f. 169°, $[\alpha]_D^{23} = -3.3°$, caractérisée comme triméthyl-5,8,8 bicyclo[3,2,1]octène-3 one-2 (VII): l'oxydation en acide camphorique et en anhydride camphorique montre que le squelette n'a subi aucune variation au cours de la dégradation; le spectre ultraviolet, par un maximum d'absorption à 233.5 mμ ($\log \epsilon = 3.95$), montre la présence d'un groupement —CO—CH=CH—; enfin l'hydrogénation catalytique (palladium) en conduisant à l'homoépicamphre (III) p.f. 197–199°, $[\alpha]_D^{23} = +136°$, établit sans ambiguité que le carbonyle est en position γ du radical méthyle placé en tête de pont. Cet homoépicamphre soutient bien la comparaison (analyse infrarouge, point de fusion de mélange, pouvoir rotatoire) avec un homoépicamphre que nous avons

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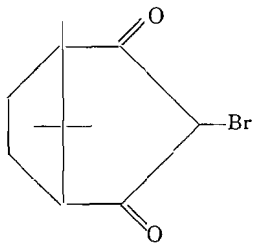
préparé selon le procédé de Salmon-Legagneur (12) et que nous prenons comme standard. Contrairement à la dégradation de l'éther p.f. 71° celle de l'isomère p.f. 56° conduit avec un bon rendement à la cétone $\alpha\beta$-éthylénique VII remarquablement pure et exempte d'isomères.

Ces dégradations font de l'isomère p.f. 71° la méthoxy-4 triméthyl-5,8,8 bicyclo[3,2,1]octène-3 one-2 (V*b*) et de l'isomère p.f. 56° la méthoxy-4 triméthyl-1,8,8 bicyclo[3,2,1]octène-3 one-2 (V*c*). Elles montrent que l'équilibre dicétonique⇄céto-énolique de la triméthyl-1,8,8 bicyclo[3,2,1]octanedione-2,4 (IV) s'établit, comme le prévoit la théorie, entre les formes IV*a* ⇄ IV*b* ⇄ IV*c*; on peut de ce fait abandonner les conclusions de Rupe et Frey (9) touchant cet équilibre.

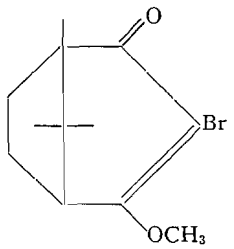
Nous avons étudié l'oximation et la bromation des deux éthers V*b* et V*c*; ces deux points qui figurent dans le mémoire de Rupe et Frey (9) demandaient à être repris, puisque ces auteurs ont considéré comme un éther pur ce qui n'était en fait qu'un mélange des éthers V*b* et V*c*.

L'éther méthylique V*b* p.f. 71° donne facilement une oxime bien cristallisable p.f. 181–183° dans des conditions opératoires ménagées, tandis que l'éther p.f. 56° ne conduit à aucun dérivé cristallisé dans des conditions identiques; il conduit en revanche à la dioxime de la dicétone IV, p.f. 209° déc., dans des conditions plus énergiques. Nous pensons que notre oxime p.f. 181–183° est identique à celle décrite par Rupe et Frey (9), p.f. 185–185.5°; ces auteurs l'avaient obtenue à partir de leur éther liquide. Nous ne pouvons par contre nous prononcer sur la nature de l'oxime p.f. 195–196° qu'ils ont préparée à partir de l'éther p.f. 56°, par suite de l'absence de données, dans leur mémoire (9), au sujet de la composition centésimale de cette oxime.

Rupe et Frey avaient conclu à l'isomérie *cis–trans* de la forme céto-énolique IV*c* et des éthers énoliques correspondants après une étude de l'action du brome sur les éthers méthyliques. Nos résultats confirment ceux de ces auteurs pour la bromation de l'éther p.f. 56° (V*c*) : on obtient bien la dicétone monobromée VIII[6] et l'éther méthylique bromé IX, dont la structure est maintenant certaine. Par contre l'éther p.f. 71° (V*b*) donne, dans des conditions expérimentales identiques, principalement la dicétone monobromée VIII et très peu d'un éther bromé (de 3 à 10% suivant les essais), liquide très instable dont nous n'avons pas poursuivi l'étude; il se transforme de lui-même en dicétone monobromée VIII.



VIII



IX

[6]*On peut envisager pour cette dicétone bromée deux formes céto-énoliques qui correspondraient aux formes IVb et IVc de la triméthyl-1,8,8 bicyclo[3,2,1]octanedione-2,4.*

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PARTIE EXPÉRIMENTALE[7]

1. Réaction du diazométhane avec la camphoquinone

1.1. Camphoquinone

Elle a été préparée à partir d'un camphre chinois en poudre, p.f. 179–180°, $[\alpha]_D^{23} = +42.6°$ ($c = 1.21$; éthanol 95%), selon le mode opératoire de Rupe et Tommasi di Vignano (11). Elle présentait les constantes suivantes : p.f. 198.5–199°, $[\alpha]_D^{23} = -106.5°$ ($c = 15$; benzène).

1.2. Séparation des éthers isomères p.f. 56° (Vc) et p.f. 71° (Vb)

Séparation A.—583 g. (99.5% de la théorie) du mélange brut résultant de la réaction de 500 g. de camphoquinone (par portions de 20 g.) avec la quantité requise de diazométhane, selon les indications de Rupe et Frey (9), furent rectifiés dans un ballon de Claisen tout en faisant passer un courant d'azote par le capillaire : (*a*) 10.1 g. p.é. jusqu'à 151°, 18 mm. (têtes) ; (*b*) 540.3 g., p.é. 151–156°, 18 mm., légèrement jaune, $[\alpha]_D^{23} = -8.8°$ ($c = 10.0$; benzène) ; (*c*) résidu, 26 g.

Séparation B.—511.8 g. de la fraction (*b*) obtenue au cours de la séparation *A* furent abandonnés à 10–12° ; au bout de quelques jours on a isolé par essorage 68.7 g. de méthoxy-4 triméthyl-1,8,8 bicyclo[3,2,1]octène-3 one-2 (V*c*) brute fondant à 48–51°, qui recristallisée dans l'éther de pétrole (p.é. 40–60°) se présente sous forme de gros prismes incolores p.f. 56°, $[\alpha]_D^{23} = -29.7°$ ($c = 4.03$; benzène) ou $-29.0°$ ($c = 10$; benzène). Calculé pour $C_{12}H_{18}O_2$: C, 74.19 ; H, 9.34%. Trouvé : C, 74.52 ; H, 9.40%. Litt. : (9) p.f. 54–55°, $[\alpha]_D^{20} = -29.3°$ ($c = 10$; benzène). *Spectre ultraviolet* : λ_{max} 250 mμ ; log ε = 4.13 (éthanol 95%). Liquide résiduel, $[\alpha]_D^{23} = -3.9°$ ($c = 10.0$; benzène).

Séparation C.—252 g. de liquide résiduel obtenu au cours de la séparation *B* après essorage furent rectifiés à travers une colonne de Vigreux, en atmosphère d'azote : fractions 1–2, 28 g., p.é. jusqu'à 83°, 0.2 mm. ; fractions 3–7, 106.5 g., p.é. de 78 à 87°, 0.2 mm. ; fractions 8–9, 43.4 g., p.é. de 82 à 88°, 0.15 mm. ; fractions 10–12, 58.3 g., p.é. de 85 à 93, 0.15 mm. ; fraction 13, 3 g., p.é. 90–93°, 0.15 mm. ; résidu, 3.1 g. Les fractions 1, 2, 8 et 9 ne se cristallisèrent pas. Les fractions 3–7 se cristallisèrent partiellement ; par essorage on a obtenu 31.9 g. de méthoxy-4 triméthyl-1,8,8 bicyclo[3,2,1]octène-3 one-2 (V*c*) brute, qui après cristallisation dans l'éther de pétrole fondait à 56°, seule ou en mélange avec l'éther p.f. 56° obtenu au cours de la séparation *B*. Les fractions 10–12 se cristallisèrent en partie ; par essorage on a obtenu 26.2 g. de fines aiguilles p.f. brut 61–67° auxquels on ajouta les 3 g. de la fraction 13 qui se cristallisa totalement, p.f. brut 65–68°. Cette méthoxy-4 triméthyl-5,8,8 bicyclo[3,2,1]octène-3 one-2 brute (V*b*) se présente, après cristallisation dans l'éther de pétrole (p.é. 40–60°), sous forme d'aiguilles incolores, p.f. 71°, $[\alpha] = {}_D^{23} +33.4°$ ($c = 4.02$; benzène) ou $+33.9°$ ($c = 10$; benzène). Calculé pour $C_{12}H_{18}O_2$: C, 74.19 ; H,

[7]*Les points de fusion (p.f.) ne sont pas corrigés; ils ont été déterminés dans un appareil de Thiele. Les spectres infrarouges ont été déterminés à l'aide d'un spectromètre "Perkin-Elmer", modèle 112, à simple faisceau et parcours double; les spectres ultraviolets à l'aide d'un spectromètre "Beckman" DU. Les analyses ont été faites, les unes par Geller Microanalytical Laboratories, Hackensack, N.J., les autres par nos soins (les valeurs sont alors marquées d'un*).*

9.34%. Trouvé: C, 74.07; H, 9.33%. *Spectre ultraviolet*: λ_{max} 253.5 mμ; log ϵ = 4.15 (éthanol 95%). Les fractions 3–7 et 10–12, débarassées de leurs cristaux, et les fractions 8 et 9, restées liquides, furent soumises à une série de quatre distillations et de quatre cristallisations faites alternativement qui permit de retirer des 252 g. initiaux: (*a*) 68 g. de l'éther V*c* pur, p.f. 56°; (*b*) 49 g. de l'éther V*b* pur, p.f. 71°.

1.3. Triméthyl-1,8,8 bicyclo[3,2,1]octanedione-2,4 (IV)

Dix grammes du mélange liquide résultant de l'action du diazométhane sur la camphoquinone, en solution dans 50 ml. d'éther, sont agités durant 12 h., à 25°, avec 50 ml. d'HCl 15%. La phase aqueuse est décantée et extraite deux fois par de l'éther. Les parties acides sont extraites des solutions éthérées réunies par 30 ml. de NaOH 10%. Par acidification de la solution alcaline par HCl conc. (rouge congo), la dicétone β se précipite. On l'essore et la lave deux fois avec un peu d'eau glacée. On obtient 7.2 g. de produit brut, p.f. 215–220°. Un échantillon a été cristallisé dans le benzène: fines aiguilles blanches, fondant à 220–222°, $[\alpha]_D^{23} = -7.7°$ (c = 4.02; benzène). Calculé pour $C_{11}H_{16}O_2$: C, 73.30; H, 8.95%. Trouvé: C, 73.53; H, 9.04%. La dicétone se sublime (11 mm., 150–160°); elle fond alors à 220–221°. Litt.: (9) p.f. 218–222°; $[\alpha]_D^{20} = -8.8°$ (c = 10; benzène); (3) p.f. 222–224°.

Dioxime.—Cristaux blancs, p.f. 209–209.5° déc., cristallisée dans l'éthanol aqueux, $[\alpha]_D^{23} = -2.0°$ (c = 1.0; éthanol anhydre; tube 4 dm.). Calculé pour $C_{11}H_{18}O_2N_2$: N, 13.33%. Trouvé: N, 13.21%*. Litt.: (9) p.f. 209° déc.

1.4. Composition du mélange réactionnel brut obtenu en 1.2

L'hydrolyse par HCl 15% de toutes les fractions liquides (provenant de la fraction (*a*) de la séparation *A*, des liquides résiduels des essorages effectuées au cours des séparations *B* et *C*) a abandonné un résidu (32 g.) non hydrolysable, liquide jaune, dont l'étude n'a pas été poursuivie. 500 g. de camphoquinone ont ainsi donné 517.6 g. (88.5% de la théorie) du mélange des éthers V*b* et V*c*; on peut estimer, par l'analyse du pouvoir rotatoire de la fraction(*b*) séparation *A*, et du mélange obtenu après essorage séparation *B*, que les pourcentages respectifs des éthers V*c* et V*b* sont les suivants: 65–68% d'éther V*c* pour 35–32% d'éther V*b*.

1.5. Action du diazométhane sur la triméthyl-1,8,8 bicyclo[3,2,1]octanedione-2,4 (IV)

A une solution de 70 g. de dicétone IV dans 500 ml. de benzène et 30 ml. de méthanol, refroidie à 6°, on ajoute une solution éthérée de diazométhane jusqu'à coloration jaune persistante. Les solvants sont distillés sous pression réduite, le résidu liquide repris par de l'éther; la solution éthérée est lavée à la soude pour éliminer la dicétone β qui n'aurait pas réagi, puis à l'eau jusqu'à neutralité. On sèche et distille l'éther. On recueille 71.6 g. (95% de la théorie) d'un liquide incolore et inodore, distillant sans laisser de résidu entre 87° et 90° sous 0.3 mm., $[\alpha]_D^{23} = 0°$ (c = 10; benzène); d'après le pouvoir rotatoire on a en main un mélange contenant 53.9% de l'éther méthylique V*c* et 46.1% de l'éther méthylique V*b*.

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Après trois distillations fractionnées (11 mm., colonne de Vigreux, atmosphère d'azote), on obtient :

(*a*) 28.5 g. d'éther V*c* brut, p.f. 48–54° montant à 56° par cristallisation ;

(*b*) 23.4 g. d'éther V*b* brut, p.f. 63–71° passant à 71° après cristallisation ;

(*c*) 12.4 g. de mélange résiduel, hydrolysé par HCl à la manière habituelle en dicétone IV.

2. Étude de la méthoxy-4 triméthyl-1,8,8 bicyclo[3,2,1]octène-3 one-2 (éther V*c*) et de la méthoxy-4 triméthyl-5,8,8 bicyclo[3,2,1]octène-3 one-2 (éther V*b*)

2.1. Hydrolyse

Mode opératoire utilisé précédemment en 1.3 :

(*a*) 0.5 g. d'éther V*c* ont donné 0.370 g. (80%) de la dicétone IV, p.f. 220–221° par sublimation. Litt. : (9) p.f. 218–222° ;

(*b*) 0.5 g. d'éther V*b* ont donné 0.355 g. (77%) de la dicétone IV, p.f. 219–220° par sublimation, ne donnant pas de dépression de p.f. en mélange avec celle obtenue en (*a*).

Dans les deux cas il n'y a pas de résidu d'hydrolyse ; nous n'avons pas cherché à récupérer la dicétone IV manquante des solutions aqueuses intervenant au cours de l'hydrolyse, ce qui explique les rendements de l'ordre de 80% ; il est possible de récupérer quantitativement la dicétone IV en extrayant les solutions aqueuses par du chloroforme.

2.2. Oximation

Méthode A.—Un mélange de 1 g. de l'éther V*b* (ou V*c*), 0.7 g. de chlorhydrate d'hydroxylamine et 1.5 ml. de pyridine anhydre est abandonné à température ambiante pendant 12 h., puis chauffé sur un bain-marie pendant une heure. Par addition d'eau :

(*a*) dans le cas de l'éther V*c* il se précipite une huile dont aucun dérivé cristallisé n'a pu être isolé ;

(*b*) dans le cas de l'éther V*b* il se forme un précipité qui recristallisé dans l'éthanol aqueux fournit l'oxime de l'éther V*b*, paillettes blanches p.f. 181–183° déc. Calculé pour $C_{12}H_{19}O_2N$: N, 6.70%. Trouvé : N, 6.87%*.

Méthode B.—Un mélange de 1 g. de l'éther V*c*, 0.7 g. de chlorhydrate d'hydroxylamine et 1.5 ml. de pyridine anhydre est chauffé sur un bain-marie durant huit heures. Après refroidissement on ajoute 1 ml. d'eau et abandonne à la glacière pendant 12 h. La dioxime de la triméthyl-1,8,8 bicyclo[3,2,1]octanedione–2,4 précipite par addition d'éther de pétrole. Après cristallisation dans l'éthanol aqueux elle fond à 209° déc., $[\alpha]_D^{23} = -1.9°$ ($c = 1.00$; éthanol anhydre ; tube 4 dm.). Elle donne une dépression de p.f. de 1° à 2° en mélange avec la dioxime préparée auparavant en 1.3 ; les spectres infrarouges (dioxime mouillée d'huile de paraffine, prisme NaCl) sont pratiquement identiques. Calculé pour $C_{11}H_{18}O_2N_2$: N, 13.33%. Trouvé : N, 13.12%*.

2.3. Bromation

Effectuée en suivant exactement les données de Rupe et Frey (9) :

(*a*) 2 g. d'éther V*c* ont donné 1.5 g. de neutres correspondant à la bromo-3 méthoxy-4 triméthyl-1,8,8 bicyclo[3,2,1]octène-3 one-2 (IX) aiguilles incolores

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cristallisées dans l'éther de pétrole (p.é. 40–60°), p.f. 103–104°, $[\alpha]_D^{23} = +30.0°$ ($c = 10.0$; benzène). Calculé pour $C_{12}H_{17}O_2Br$: Br, 29.26%. Trouvé: Br, 29.00%. Litt.: (9) p.f. 104°. *Spectre ultraviolet*: λ_{max} 275 mμ; log ε = 4.05 (éthanol 95%), et 1 g. de parties acides (bromo-3 triméthyl-1,8,8 bicyclo[3,2,1] octanedione-2,4 (VIII)), p.f. 188–189°. Litt.: (9) p.f. 187–188°.

(*b*) 4 g. d'éther V*b* ont donné 4.64 g. de dicétone monobromée VIII, p.f. 188–189°, et 0.2 g. de parties neutres, liquide jaune pâle, ne se cristallisant pas et se décomposant rapidement pour donner la dicétone monobromée p.f. 188–189°. Le pourcentage de parties neutres variait légèrement (de 3 à 10%) dans les quelques essais effectués.

2.4. Dégradation de l'éther Vc

2.41. Triméthyl-5,8,8 bicyclo[3,2,1]octène-3 one-2 (VII)

Une solution de 20 g. (0.1 mole) de l'éther V*c* dans 100 ml. d'oxyde d'éthyle anhydre est introduite goutte à goutte, sous bonne agitation, à 3.4 g. (0.09 mole) de $LiAlH_4$ finement pulvérisé en suspension dans 200 ml. d'oxyde d'éthyle anhydre. On chauffe ensuite 30 min. à l'ébullition à reflux, puis, en refroidissant à 0°, on ajoute 16 ml. d'eau. Le tout est alors versé sur 44 g. de glace concassée; on ajoute lentement, en agitant, 60 ml. d'H_2SO_4 conc., de façon à ce que la température du mélange en réaction ne dépasse pas −6° (durée de l'opération : de cinq à six heures). La couche aqueuse est décantée et extraite par de l'éther; les solutions éthérées réunies sont lavées à l'eau, au carbonate de sodium et à l'eau jusqu'à neutralité. On sèche et évapore très lentement l'éther à travers une colonne de Widmer. On recueille 16.6 g. (98 % de la théorie) d'un solide blanc, à odeur camphrée, très facilement sublimable. Après une sublimation on a : (*a*) 15.6 g. (92%) de triméthyl-5,8,8 bicyclo[3,2,1] octène-3 one-2, p.f. 167.5–169°, $[\alpha]_D^{23} = -1.5°$ ($c = 4.08$; benzène); (*b*) 1 g. d'un composé p.f. supérieur à 220° que l'on écarte. 6.468 g. de la fraction (*a*), par chromatographie sur 198 g. d'alumine (alumine Merck pour chromatographie), donnent : fraction 1, 0.199 g. d'huile éluée par de l'éther de pétrole; fractions 2–45, 5.357 g. (83%) de triméthyl-5,8,8 bicyclo[3,2,1]octène-3 one-2 (VII) dont un échantillon analytique présente les constantes suivantes : p.f. 169°, $[\alpha]_D^{23} = -3.3°$ ($c = 4.01$; benzène). Calculé pour $C_{11}H_{16}O$: C, 80.44; H, 9.82%. Trouvé : 80.15; H, 9.86%. *Spectre ultraviolet*: λ_{max} 233.5 mμ; log ε = 3.95 (éthanol 95%).

Oxime.—Cristallise en aiguilles blanches dans le méthanol aqueux, p.f. 91°. Calculé pour $C_{11}H_{17}ON$: C, 73.70; H, 9.56; N, 7.82. Trouvé : C, 73.37; H, 9.76; N, 7.90%*.

Dinitro-2,4 phénylhydrazone.—Cristallisée dans le méthanol; paillettes rouges, p.f. 167–167.5°. Calculé pour $C_{17}H_{20}O_4N_4$: C, 59.29; H, 5.85; N, 16.27%. Trouvé : C, 59.38; H, 5.86; N, 16.41%*.

Semimicro-hydrogénation.—164 mg. de la cétone VII, dans 8 ml. d'éthanol 95%, ont fixé 24.8 ml. d'hydrogène en présence de 150 mg. d'un catalyseur de palladium sur carbonate de calcium (2%) hydrogéné au préalable. Calculé : 24.8 ml. (748 mm., 25°).

Oxydation.—On ajoute à 0.5 g. de cétone VII en solution dans 1.5 ml. d'acide

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acétique glacial 13.8 ml. d'une solution préparée en dissolvant 4 g. de CrO_3 dans 20 ml. d'acide acétique glacial et 4 ml. d'eau. On chauffe 30 min. sur un bain-marie, laisse reposer 12 h. puis verse sur de l'eau. On extrait soigneusement à l'éther, on sèche la couche éthérée évapore l'éther à pression ordinaire et la plus grande partie de l'acide acétique sous vide. On reprend alors par de l'éther et sépare le mélange en parties acides et parties neutres, à la manière habituelle. On isole 148 mg. d'acide camphorique p.f. 182.5–183°, seul ou en mélange avec de l'acide camphorique authentique, et 238 mg. de parties neutres dont on retire par dissolution fractionnée dans l'éther de pétrole 24 mg. d'anhydride camphorique p.f. 218–222°, seul ou en mélange avec de l'anhydride camphorique authentique.

2.42. Homoépicamphre (III)

Un gramme de cétone $\alpha\beta$-éthylénique VII, $[\alpha]_D^{23} = -3.3°$ ($c = 4.01$; benzène), dans 35 ml. d'éthanol 95% sont agités dans de l'hydrogène en présence de 750 mg. de catalyseur ($Pd/CaCO_3$, 2%). En 80 min. 160 ml. d'H_2 sont fixés (calculé: 152 ml., 747 mm., 25°). Après distillation très lente de l'alcool à travers une colonne de Widmer on retrouve 890 mg. (89% de la théorie) d'homoépicamphre qui après sublimation présente les constantes suivantes: p.f. 197–199°, $[\alpha]_D^{23} = +136.0°$ ($c = 4.0$; benzène). Calculé pour $C_{11}H_{18}O$: C, 79.46; H, 10.91%. Trouvé: C, 79.40, 79.19; H, 10.97, 11.12%. Il n'y a pas d'abaissement du p.f. de ce composé en mélange avec un homoépicamphre analytiquement pur préparé selon la méthode de Salmon-Legagneur p.f. 198.5–199°, $[\alpha]_D^{23} = +130.7°$ ($c = 4.02$; benzène). Salmon-Legagneur indique (12): p.f. 202–204°, $[\alpha]_D^{20} = +130.3°$ ($c = 7.862$; benzène). Les spectres infrarouges des deux cétones sont identiques; la bande C=O apparaît à 1716 $cm.^{-1}$ (fluorolube, prisme NaCl ou CaF_2).

Oxime.—Obtenue en chauffant à l'ébullition à reflux l'homoépicamphre avec du chlorhydrate d'hydroxylamine dans de l'alcool aqueux contenant 2% d'hydroxyde de sodium; elle cristallise en fines aiguilles blanches p.f. 104–105°, $[\alpha]_D^{23} = +124°$ ($c = 3.9$; benzène). Calculé pour $C_{11}H_{19}ON$: N, 7.74%. Trouvé: N, 7.54%*. Cette oxime ne donne pas de dépression de p.f. en mélange avec l'oxime préparée dans des conditions identiques à partir de l'homoépicamphre obtenu selon Salmon-Legagneur. Alors que Salmon-Legagneur (12) indique pour cette oxime $[\alpha]_D^{24} = +108.5°$ ($c = 3.87$; méthanol) nous avons trouvé $[\alpha]_D^{23} = +125.6°$ ($c = 3.91$; méthanol); le p.f. est pourtant bien de 104–105° comme indiqué dans le mémoire (12).

Dinitro-2,4 phénylhydrazone.—Cristallisée dans un mélange d'éthanol et d'acétate d'éthyle; paillettes orange p.f. 178°. Calculé pour $C_{17}H_{22}O_4N_4$: N, 16.18%. Trouvé: N, 16.03%*.

2.5. Dégradation de l'éther Vb

2.51. Triméthyl-1,8,8 bicyclo[3,2,1]octène-3 one-2 (VI)

Le mode opératoire est le même que celui décrit en 2.41. 27.7 g. (0.143 mole) de l'éther *Vb* sont réduits par 4.7 g. (0.123 mole) de $LiAlH_4$. Après déshydratation par l'acide sulfurique conc. (83 ml.) et extraction on obtient 22.2 g.

(95% de la théorie) de triméthyl-1,8,8 bicyclo[3,2,1]octène-3 one-2 brute, p.f. 178–180°, $[\alpha]_D^{23} = -52.9°$ ($c = 10.0$; benzène). 20.9 g. de la cétone brute sont sublimés plusieurs fois sous 8–10 mm., à 120–130°; les diverses fractions sont rassemblées en deux fractions principales: fraction *A*—15.4 g. comprenant les fractions p.f. 176–178°, pouvoir rotatoire voisin de −58°, et les fractions p.f. 177–179°, pouvoir rotatoire voisin de −56°; fraction *B*—5.21 g. très nombreuses fractions dont les p.f. sont compris entre 165 et 205°.

La chromatographie sur alumine (alumine Merck pour chromatographie) de 10.2 g. provenant de la fraction *A* donne: 1.289 g. p.f. 173°, $[\alpha]_D^{23} = -67.4°$ (élution par l'éther de pétrole); 6.153 g. de triméthyl-1,8,8 bicyclo[3,2,1]octène-3 one-2 (VI) (élution par l'éther de pétrole); 1.7 g. comprenant diverses fractions, huiles dont le pouvoir rotatoire varie entre −50° et +27°.[8]

La triméthyl-1,8,8 bicyclo[3,2,1]octène-3 one-2 fond à 174–176°, $[\alpha]_D^{23} = -55.3°$ ($c = 5.14$; benzène). Calculé pour $C_{11}H_{16}O$: C, 80.44; H, 9.82%. Trouvé: C, 80.36; H, 9.91%. Litt.: (9) p.f. 173–175°, $[\alpha]_D^{20} = -51.9°$ ($c = 10$; benzène). *Spectre ultraviolet*: λ_{max} 231 mμ; log ε = 3.98 (éthanol 95%).

Oxime.—Fines aiguilles incolores, cristallisées dans l'éthanol aqueux, p.f. 146–147°, $[\alpha]_D^{23} = -104.2°$ ($c = 3.49$; méthanol). Calculé pour $C_{11}H_{17}ON$: N, 7.82%. Trouvé: N, 7.92%*. Litt.: (9) p.f. 143.5–145°.

Dinitro-2,4 phénylhydrazone.—Paillettes rouge-orangé, cristallisées dans un mélange d'acide acétique et de méthanol, p.f. 197–198.5°. Calculé pour $C_{17}H_{20}O_4N_4$: N, 16.27%. Trouvé: N, 16.03%*. Litt.: (9) p.f. 181–184°.

Semimicro-hydrogénation.—159.8 mg. de triméthyl-1,8,8 bicyclo[3,2,1]octène-3 one-2 en solution dans 8 ml. d'éthanol 95%, en présence de 150 mg. de catalyseur (palladium/carbonate de calcium, 2%) hydrogéné au préalable, ont fixé 24.2 ml. d'H_2; calculé pour 1 H_2: 24.0 ml. (755 mm., 25°).

Oxydation.—Mode opératoire, comme en 2.41. 1 g. de triméthyl-1,8,8 bicyclo[3,2,1]octène-3 one-2 ont donné 400 mg. d'acide camphorique p.f. 185° et 15 mg. d'anhydride camphorique p.f. 218–220°. Identité prouvée par p.f. de mélange.

2.52. Homocamphre (II)

(A) La semimicro hydrogénation de la triméthyl-1,8,8 bicyclo[3,2,1]octène-3 one-2, $[\alpha]_D^{23} = -55.3°$ ($c = 5.14$; benzène), décrite en 2.51 conduit à un homocamphre qui présente les constantes suivantes: p.f. 187–190°, $[\alpha]_D^{23} = -108.9°$ ($c = 4.08$; benzène). Calculé pour $C_{11}H_{18}O$: C, 79.46; H, 10.91. Trouvé: C, 79.66, 79.70; H, 10.93, 11.14%. Il n'y a pas de dépression de p.f. lorsque cet homocamphre est mélangé avec un homocamphre préparé selon Lapworth et Royle (4); ce dernier présente les constantes suivantes p.f. 191–193°, $[\alpha]_D^{23} = -111.9°$ ($c = 3.41$; benzène), déterminées sur un composé analytiquement pur. Lapworth et Royle indiquent: p.f. 189–190°; $[\alpha]_D = -112.9°$ ($c = 4.0$; benzène). Les spectres infrarouges des homocamphres préparés par les deux méthodes sont identiques; la bande C=O apparaît à 1709 $cm.^{-1}$ (fluorolube).

Oxime.—p.f. 166.5–167.5°. Litt.: (4) p.f. 167–168°; (9) p.f. 165°.

Dinitro-2,4 phénylhydrazone.—p.f. 238–239°. Litt.: (5) p.f. 232°; (9) p.f. 232–233°.

[8]*Pouvoirs rotatoires déterminés en solution benzénique, c = 4.0.*

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(B) 7.8 g. de triméthyl-1,8,8 bicyclo[3,2,1]octène-3 one-2, de pouvoir rotatoire voisin de $-67°$ ($c = 4$; benzène) sont dissous dans 80 ml. d'éthanol 95% et secoués en atmosphère d'hydrogène en présence de 7.5 g. de catalyseur (palladium/carbonate de calcium, 2%). 850 ml. d'H_2 sont fixés en 50 minutes; calculé pour 1 H_2: 1175 ml. (753 mm., 25°). On isole à la manière habituelle 7.2 g. (92% de la théorie) d'homocamphre brut qu'une chromatographie sur alumine (alumine Merck pour chromatographie) permet de séparer en: (*a*) 4.99 g. de solide de pouvoir rotatoire variant entre -121 et $-129°$ ($c = 4$; benzène); (*b*) 2.37 g. fractions liquides. 4.4 g. de la fraction obtenue en (*a*) dans 30 ml. d'éthanol sont traités par 5.4 g. de chlorhydrate de semicarbazide et 8.0 g. d'acétate de sodium dans 15 ml. d'eau à l'ébullition à reflux pendant quatre heures. On obtient après refroidissement à 0° 2.49 g. de semicarbazone brute p.f. 257–259°[9] et 2.58 g. de cétone qui n'a pas réagi. La semicarbazone brute est cristallisée dans l'éthanol aqueux et fractionnée en:

(*a*) Poudre microcristalline p.f. 240–242° qui par hydrolyse par HCl conc. (selon (4)) fournit un homocamphre p.f. 196–197.5°, $[\alpha]_D^{23} = -122°$ ($c = 3.75$; benzène). Calculé pour $C_{11}H_{18}O$: C, 79.46; H, 10.91%. Trouvé: C, 79.17; H, 10.77%. *Spectre infrarouge* (huile de paraffine): pratiquement identique à celui de l'homocamphre dont $[\alpha]_D^{23} = -111.9$ (benzène).

(*b*) Poudre microcristalline p.f. 275° qui par hydrolyse par HCl conc. conduit à un homocamphre p.f. 193.5–195°, $[\alpha]_D^{23} = -152.4°$ ($c = 3.27$; benzène). Calculé pour $C_{11}H_{18}O$: C, 79.46; H, 10.91%. Trouvé: C, 78.97; H, 10.72%. *Spectre infrarouge* (huile de paraffine): pratiquement identique à celui obtenu en (*a*).

2.53. Points de fusion de mélange

Déterminés sur des mélanges 1:1. Homocamphre p.f. 191–193°—homo-épicamphre p.f. 197–199°: fondent à 194°. Cétone VI p.f. 174–176°—cétone VII p.f. 169°: fondent à 172–172.5°.

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[9]*Lapworth et Royle donnent pour la semicarbazone pure de l'homocamphre: p.f. 250–252° (4).*

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LIGHT ABSORPTION STUDIES

PART III. STRUCTURE AND LIGHT ABSORPTION OF TRISUBSTITUTED BENZENE DERIVATIVES[1]

By W. F. Forbes and W. A. Mueller

ABSTRACT

The spectra of a number of trisubstituted benzene derivatives which have recently been described by Doub and Vandenbelt are discussed in terms of the electronic and steric effects. The assumption of Doub and Vandenbelt, that the steric effects are usually small in absorption spectra, is criticized.

INTRODUCTION

In a recent publication, Doub and Vandenbelt (9) have recorded the ultraviolet light absorption properties of a number of trisubstituted benzene derivatives and discussed these assuming that steric effects are usually small in absorption spectra. Doub and Vandenbelt chose β-resorcylic acid (2,4-dihydroxybenzoic acid) as a representative example and conclude that its spectrum can be explained from the three constituent disubstituted compounds, namely salicylic acid, resorcinol, and *p*-hydroxybenzoic acid. They suggest that the first primary band of salicylic acid (λ_{max} 237 mμ) has no analogue in the spectrum of β-resorcylic acid and note that the inflection (secondary band) of *p*-hydroxybenzoic acid disappears in the spectrum of the trisubstituted compound. More generally they note that frequently the secondary and first primary bands of constituent compounds do not appear at all in the spectrum of the trisubstituted compound.

We have recently reported (10, 11) the spectral properties of a series of substituted acetophenones and benzoic acids, and have shown that the absorption properties exhibited by most *ortho*-substituted benzene derivatives can be explained in terms of steric interference between the two substituents. This work itself was based on a series of previous papers (for example 2, 3, 14).

The present communication re-examines the spectra of some of the trisubstituted benzene derivatives in the light of these hypotheses of steric hindrance.

ULTRAVIOLET ABSORPTION SPECTRA

First Primary Band (B-band)

Our assumptions are as follows:

(i) *ortho*-Disubstituted benzene derivatives in neutral solution would have approximately the same spectra as *para*-isomers but for steric hindrance of resonance (see Table I).

(ii) Ultraviolet light absorption is very sensitive to steric effects: (*a*) slight steric effects give rise to intensity changes *only*; (*b*) larger steric effects give rise

[1]*Manuscript received November 9, 1955.*
Contribution from the Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland. This paper is dedicated to the memory of the late Professor E. A. Braude, D. Sc., F.R.I.C.

to wave-length changes accompanied by changes in the intensity of absorption; this type of steric effect occurs most frequently (see Table II); (*c*) large type steric effects inhibit conjugation almost completely and the molecule absorbs as two distinct entities.

TABLE I

ABSORPTION SPECTRA OF ORTHO- AND PARA-SUBSTITUTED COMPOUNDS IN ABSOLUTE ETHANOL, STERIC EFFECTS ABSENT OR SMALL

Wave-lengths and intensities of the B-band maxima

Compound	Position of substituent			
	Ortho		Para	
	$\lambda_{max.}$, mμ	ϵ_{max}	$\lambda_{max.}$, mμ	ϵ_{max}
Fluoroacetanilide*	239	12,600	240	13,100
Methylbenzaldehyde†	251	13,000	251	15,000

*Ref. 19.
†Ref. 3.

TABLE II

ABSORPTION SPECTRA OF ORTHO- AND PARA-SUBSTITUTED COMPOUNDS IN ABSOLUTE ETHANOL, STERIC EFFECTS PRESENT

Wave-lengths and intensities of the B-band maxima

Compound	Position of substituent			
	Ortho		Para	
	$\lambda_{max.}$, mμ	ϵ_{max}	$\lambda_{max.}$, mμ	ϵ_{max}
Fluorobenzoic acid*	223	9,500	228	11,000
Toluic acid†	228	5,000	236	14,000
Hydroxybenzoic acid†	236	7,500	251	12,500
Anisic acid†	230	6,000	258	11,000
Methylacetanilide‡	230	6,500	245	15,000
Chloroacetanilide‡	240	10,500	249	18,000
Bromoacetanilide‡	234	7,500	252	18,500
Methoxyacetanilide‡	244	10,500	249	15,000
Methylacetophenone§	242	8,500	252	15,000

*Part II, Ref. 11.
†Values in 95% ethanol, Ref. 17.
‡Ref. 19.
§Part I, Ref. 10.

The first assumption is important because later comparisons are based on it, and it is apparently not accepted by Doub and Vandenbelt. Our contention, however, is that it is correct, although not readily obvious, because light absorption properties are such a sensitive indication of steric hindrance. Thus very few *ortho*-substituted benzene derivatives will show a complete absence of steric effects, and similar spectra in *ortho*- and *para*-compounds are only obtained or nearly obtained where the substituent is unusually small (see

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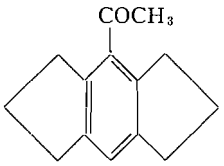
Table I). Trisubstituted benzene derivatives of the type discussed by Doub and Vandenbelt will therefore almost invariably give rise to appreciable steric effects.

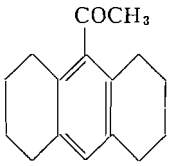
Our second supposition, or rather part (*b*) thereof, is however the key to a more complete understanding of the spectra of this type of derivative and will therefore be now discussed rather more fully. The type of change mentioned—wave-length changes to shorter wave-length accompanied by decreased absorption intensity—is almost the "hallmark" of steric interference in the first primary absorption band of spectra involving the interaction of π–π electrons. Not only does it occur widely in substituted benzene derivatives (see Table II for a few examples), but it is also generally accepted as the explanation of the observed spectra of diphenyls which have been investigated and discussed in some detail by Rodebush and others (3, 4, 12, 16, 18, 20).

Diphenyl absorbs at 249 mμ, ϵ = 15,000, while *o*-methyldiphenyl absorbs at 237 mμ, ϵ = 10,500 (steric effect of type (*b*)). In *o*-*o'*-ditolyl the B-band almost completely vanishes and the absorption closely resembles that of toluene. The latter may be taken as an example of a steric effect of type (*c*), an effect which also may account for the disappearance of some of the bands of partial chromophores in trisubstituted benzene derivatives. Complete disappearance of a band may, however, require a second *ortho*-substituent (we are grateful to a referee of Part II (11) for drawing our attention to a paper by Klevens and Platt (15) who have made this observation in their study of *ortho*-substituted N,N-dimethylanilines).

Any explanation of these observed changes, based entirely on electrical effects, must be ruled out, since the B-bands of the spectra of 4-acetylhydrindacene (I) and 9-acetyloctahydroanthracene (II), for example, are entirely dissimilar (10). On the basis of electrical effects alone, they would be expected to have similar properties.



I, λ_{max} 252 mμ, ϵ = 7000



II, λ_{infl} 220 mμ, ϵ = 10,000

The application of these principles to trisubstituted benzene derivatives can now be attempted and following Doub and Vandenbelt we shall discuss in detail the spectrum of β-resorcylic acid and related compounds. These are listed in Table III.

We have assumed that, as a result of steric interference, conjugation between the two parts of the molecule is decreased; hence a hypsochromic shift accompanied by reduced absorption intensity, relative to the corresponding *para*-substituted compound, is observed. In this manner, the position of the primary band of salicylic acid with respect to *p*-hydroxybenzoic acid may be satisfactorily explained. Salicylic acid may therefore not be directly compared

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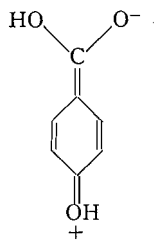
TABLE III

MAIN ABSORPTION MAXIMA OF β-RESORCYLIC ACID AND RELATED COMPOUNDS IN 0.1 *N* HCl

	λ_{max}, mμ	ϵ_{max}		λ_{max}, mμ	ϵ_{max}
Benzoic acid† (in ethanol)	227 271	11,000 760	Salicylic acid*	237 303	9,000 3,600
p-Hydroxybenzoic acid*	255 273 (inflection)	14,100	β-Resorcylic acid*	256 295	13,600 5,500

*Ref. 9.
†Part II, Ref. 11.

with benzoic acid, since then the electrical effect of the OH-substituent, which increases resonance contributions of type III, would be neglected. Therefore salicylic acid compared to benzoic acid gives rise to a slight bathochromic shift, while compared to *p*-hydroxybenzoic acid the expected hypsochromic shift is observed. The analogue of the 237 mμ band in salicylic acid is therefore the 255 mμ band of *p*-hydroxybenzoic acid, which has been shown to be almost



III

identical with the 256 mμ band of β-resorcylic acid (see Table III). The almost identical character of the last two compounds suggests that in β-resorcylic acid the *ortho*-hydroxyl group does not contribute appreciably to the observed spectrum, but exact comparison is not possible, since the exact reference compound, which would require two non-interfering hydroxyl groups in the *para*-position, does not exist.

It would be an oversimplification, however, to say that in β-resorcylic acid the carboxyl group is subject to about the same steric interference from the *ortho*-hydroxyl group as that prevailing in salicylic acid. This would not take into account the increased double bond character of the carbon–carbon link joining the carboxyl group to the benzene ring, due to resonance contributions of type III. The sensitivity of this B-band to increased double-bond character has already been briefly discussed (10) in connection with the spectra of 2,4,6-trimethyl- and 2,3,4,5,6-pentamethyl-acetophenones compared to 2,6-dimethyl- and 2,3,5,6-tetramethyl-acetophenones.

It would similarly be erroneous to conclude that since the first primary band of β-resorcylic acid very nearly coincides with that of *p*-hydroxybenzoic acid, steric effects must be small. This similarity of bands may be fortuitous,

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since it is not always observed, and in β-resorcylic acid, compared to *p*-hydroxybenzoic acid, and also in similar types of compounds, two opposing effects operate, which may cancel out. These are, on the one hand, the electrical effect of the hydroxyl group, which will tend to change the wave-length of maximal absorption towards longer wave-length accompanied by increased absorption intensity, and on the other, the steric effect which will act in exactly the opposite manner. Furthermore, as expected for a number of compounds, the steric effect is so prominent compared with the electrical effect as to be readily identified. For example, *p*-chlorobenzoic acid in acid solution absorbs maximally at 241 mμ, $\epsilon = 16{,}300$ (8), while 2,4-dichlorobenzoic acid in acid solution absorbs maximally at 232 mμ, $\epsilon = 7400$ (9). Since steric effects have been postulated to be almost always present, even in the *absence* of a *para*-substituent, one would expect that in the *presence* of a *para*-substituent steric effects on the *ortho*-substituent would almost always be quite large. This follows immediately from the consideration that considerably more energy is required to twist a double bond than is required to twist a single bond (13). Hence the steric effect will be the larger of the two opposing effects and thus trisubstituted benzene derivatives will normally exhibit either a first primary band similar to that of the most displaced band of the constituent compounds or more frequently this same band with a detectable steric effect. Lastly, the steric effect may become so large that the *ortho*-substituent is completely dislodged from the plane of the benzene ring and will then not at all contribute to the observed band. The B-band of the trisubstituted compound will then agree closely with the B-band of the *para*-disubstituted compound, which has in fact been observed by Doub and Vandenbelt (9).

These data therefore reasonably conclusively point to steric phenomena as one of the two main factors towards a general explanation of the location of maximal absorption of the B-band, and in particular are in agreement with our assumptions as stated above.

Secondary Band (C-band)

Although a more general explanation must await the results of further experimental work which is in progress, certain statements about steric effects in C-bands appear justified. These are:

(i) Steric effects can be detected in this band.

(ii) These steric effects are different, inasmuch as apparently (*a*) the C-band is comparatively insensitive to small steric effects; (*b*) larger steric effects are readily apparent, but again different from the steric effects observed in the B-band.

One illustration of this is provided by the sensitiveness to hydrogen-bonding. In the B-band, the evidence for hydrogen-bonding is somewhat inconclusive. In the C-band, however, *ortho*-hydroxy acetophenones and benzoic acids, compared to the corresponding methoxy-compounds, give rise to a much more pronounced effect (see Table IV). It is noted that hydrogen-bonding gives rise to a more pronounced band at longer wave-length, possibly because of

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TABLE IV

MAIN ABSORPTION MAXIMA OF SALICYLIC ACID AND RELATED COMPOUNDS IN DIETHYL ETHER (6)

Substituent	Acetophenone				Benzoic acid			
	λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}
2-Hydroxy	251	9,700	327	3800	237	7,800	307	4400
4-Hydroxy	267	19,100	—	—	251	18,300	—	—
2-Methoxy	246	8,000	306	2600	~230	8,100	291	3500
4-Methoxy	266	18,000	—	—	251	18,300	—	—

increased rigidity of the molecule. This would also explain the more displaced position of the secondary band of salicylic acid and β-resorcylic acid compared to that of benzoic acid and *p*-hydroxybenzoic acid respectively.

An anomaly, or apparent anomaly, however, might be thought to exist, since salicylic acid compared to *p*-hydroxybenzoic acid exhibits opposite effects in the primary and secondary bands. Therefore, one might argue, if salicylic acid has been postulated to be non-planar, is not planarity now invoked to account for the hydrogen-bond effect? This objection, however, is not valid, since it was stated above (postulate (ii) (*a*)) that the C-band is not sensitive to small steric effects. Hence while the non-planarity might be sufficient to give rise to the B-band effect, it would not be sufficient to upset the typical hydrogen-bonding effect. In other words, although the hydrogen-bond effect in the C-band may be due to increased planarity it does not mean that the increased planarity gives rise to a wholly planar molecule. Furthermore, there is no reason for steric and hydrogen-bond interactions to give rise to identical effects in the B- and C-bands.

Another objection which might be raised is the planarity of salicylic acid in the solid state (5), but to counter this it must be borne in mind that planarity in the solid state does not necessarily involve planarity in the liquid state. For example, diphenyl has been shown to be planar in the solid state also (7), while electron-diffraction data, which have the advantage of giving data concerning the *isolated* molecule, indicate an interplanar angle of 45°±10° (1).

Further it seems important to avoid the conclusion that the B-band is associated with separation of charge in the *para*-positions of the excited state and the secondary band with charge separations in the *ortho*-positions. For many compounds this suggestion is quite untenable, and even in favorable instances such as might appear to be provided by the salicylic acid spectra, the hypothesis breaks down. For example, the C-band of salicylic acid should clearly be similar to that of β-resorcylic acid (see Table III).

ACKNOWLEDGMENTS

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LIGHT ABSORPTION STUDIES

PART IV. THE EFFECTS OF STERICALLY HINDERED CONFORMATIONS ON THE ELECTRONIC SPECTRA (B-BANDS) OF CONJUGATED SYSTEMS[1]

By W. F. Forbes and W. A. Mueller

ABSTRACT

The equation $\epsilon/\epsilon_0 = \cos^2(\theta_1-\theta_2)$ recently proposed by Braude and co-workers is developed to account more rigorously for the spectra of unsymmetrical molecules. The results obtained from the revised equation, $\epsilon/\epsilon_0 = \frac{1}{2}[\cos^2(\theta_1-\theta_2)+\cos^2(\theta_3-\theta_4)]$, support the interference value of hydrogen obtained independently from spectral data, and suggest a re-examination of the reported theories accounting for the spectra of alicyclic enones and dienones, and for steric effects of type I.

INTRODUCTION

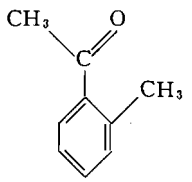
In a recent series of papers, Braude and his collaborators (1, 3, 4, 6) have developed the equation $\epsilon/\epsilon_0 = \cos^2(\theta_1-\theta_2)$ to obtain the value of the interplanar angle from spectral data in sterically hindered compounds. The literature cited in one of these papers (1) reflects the uncertainty which currently prevails concerning the correct assignment of interplanar angles in even diphenyl itself, the spectrum of which has been discussed by a large number of workers. A single equation which could be used to give the roughly correct interplanar angle for a variety of conjugated molecules would therefore be of great significance, and the series of papers by Braude and co-workers in fact provide such an equation.

We are in almost complete agreement with the proposed equation, but have also independently arrived at two conclusions, which lead us to suggest a further development of the above-mentioned equation. These conclusions are that, firstly, our value obtained for the interference value of the hydrogen atom is somewhat larger than that assumed by Braude and co-workers, who accept a value of 0.60 Å for hydrogen. Our own value for hydrogen, the justification of which will be reported in a separate communication, is 0.95 Å, which suggests larger interplanar angles for certain steric conformations than have hitherto been supposed. Our second conclusion concerns our discussion of the spectra of 2-methylacetophenone and 2-methylpropiophenone (7), in which we have considered 2-methylacetophenone, for example, to exist in two different conformations,* IA and IB, which by analogy with the cyclohexenones (see below), we shall refer to as the *s-cis* and *s-trans* forms. We then (7) tentatively concluded that the absorption of 2-methylacetophenone and similar compounds is due to transitions involving chiefly the *s-cis* form (IA). By combining this suggestion with the original formula we are now able to put forward a more complete explanation concerning the mechanism of absorption in sterically hindered conjugated compounds.

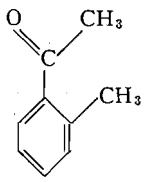
[1]*Manuscript received February 24, 1956.*

Contribution from the Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland. This paper is dedicated to the memory of the late Professor E. A. Braude, D.Sc., F.R.I.C.

**Following Braude (6) we use the terms "configuration" and "conformation" respectively in connection with stereoisomerism involving energy barriers greater and smaller, respectively, than ca. 20 kcal./mole.*



IA
(*s-cis*)



IB
(*s-trans*)

ULTRAVIOLET ABSORPTION SPECTRA AND STERIC CONFORMATIONS

In compounds where the interaction energies of the *s-cis* and *s-trans* forms are identical, for instance the symmetrically substituted acetophenones and benzaldehydes (see Fig. 1) or the *ortho*-substituted diphenyls, we accept the original equation, since considering either *s-cis* or *s-trans* forms, the values of θ_1 and θ_3 will be identical and hence the equation will apply to both forms. It is thus not necessary to consider each form independently.

The same considerations, however, will not apply to molecules like 2-methylbenzaldehyde and 2-methylacetophenone in which the fraction of molecules absorbing in the *s-cis* and the *s-trans* form will not be identical. If we accept the function $\cos^2(\theta_1-\theta_2)$ to be a reasonable measure of the fraction of all molecules in either the *s-cis* or the *s-trans* form undergoing the electronic transition, and then take the average, the simplest equation to combine these two equations is:

$$[1] \qquad \epsilon/\epsilon_0 = \tfrac{1}{2}\{\cos^2(\theta_1-\theta_2)+\cos^2(\theta_3-\theta_4)\},$$

where θ_3 and θ_4 represent the interplanar angles of the ground and excited states respectively of the *s*-form not previously considered. If we further make the additional assumption with Braude that θ_2 and θ_4 are $\sim 0°$, we obtain:

$$[2] \qquad \epsilon/\epsilon_0 = \tfrac{1}{2}(\cos^2\theta_1-\cos^2\theta_3).$$

Since a full definition of all the terms used and their justification has been given in the series of papers already referred to (1, 3, 4, 6), we have confined ourselves to a schematic representation of the electronic transitions for three typical compounds, 2,6-dimethylbenzaldehyde, 2-methylbenzaldehyde, and 2-methylacetophenone (see Figs. 1, 2, and 3), to illustrate our modification. We have included in our figures also another schematic illustration to suggest the possible transitions from various ground states with different interplanar angles. By plotting interplanar angles against probability of absorption, we intend to show the most probable positions in which a molecule in the ground state can absorb light.

While no attempt has been made at this stage to obtain more than a qualitative relationship, we have assumed that in a hindered conformation on approaching coplanarity, the repulsion energy becomes somewhat larger than the gain of energy due to increased resonance. Thus the probability of transition will fall off more sharply as the interplanar angle approaches a planar sterically hindered form than in other directions. We have illustrated this in Figs. 1, 2, and 3, by a steeper slope of the curve in that part of the graph, and also in Fig. 4, using the same diagram as proposed by Braude and Timmons (6).

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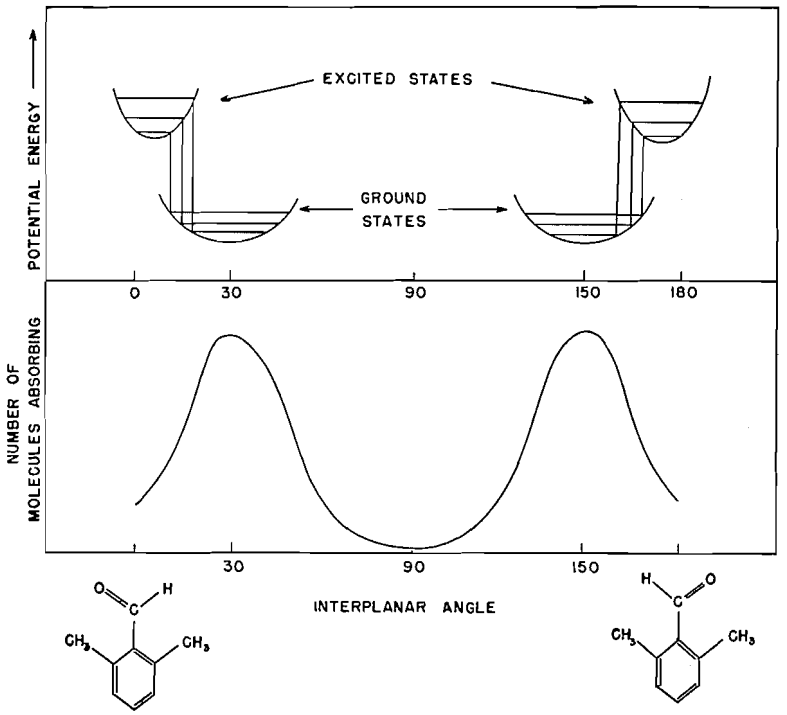

FIG. 1. *Top.*—Schematic representation of electronic transitions between ground and excited states in 2,6-dimethylbenzaldehyde.

Bottom.—Distribution curve for ground state molecules of 2,6-dimethylbenzaldehyde contributing to the observed absorption.

The results obtained from Equation [1] for the new mean interplanar angles of both *s-cis* and *s-trans* forms and the corresponding values obtained by Braude and co-workers are listed in Table I.

It is noted that where different angles are obtained, the differences are not unduly large, and for many of the examples cited (all the symmetrical molecules) the values are of course identical. A number of interesting observations,

TABLE I

INTERPLANAR ANGLES DEDUCED FROM STERIC EFFECTS IN ORTHO-ALKYLATED BENZALDEHYDES AND ACETOPHENONES

Compound	ϵ/ϵ_0	Our values		Comparison value of Braude *et al.* (3)
		s-cis	*s-trans*	
4-Methylbenzaldehyde	1.00	0°	0°	0°
2-Methylbenzaldehyde	0.87	31°	0°	21°
2,4-Dimethylbenzaldehyde	0.94	20°	0°	—
2,6-Dimethylbenzaldehyde	0.78	28°	28°	28°
4-Methylacetophenone	1.00	0°	0°	0°
2-Methylacetophenone	0.58	50°	31°	40°
2,4-Dimethylacetophenone	0.85	25°	20°	24°
2,6-Dimethylacetophenone	0.34	55°	55°	55°
2,4,6-Trimethylacetophenone	0.20	63°	63°	63°

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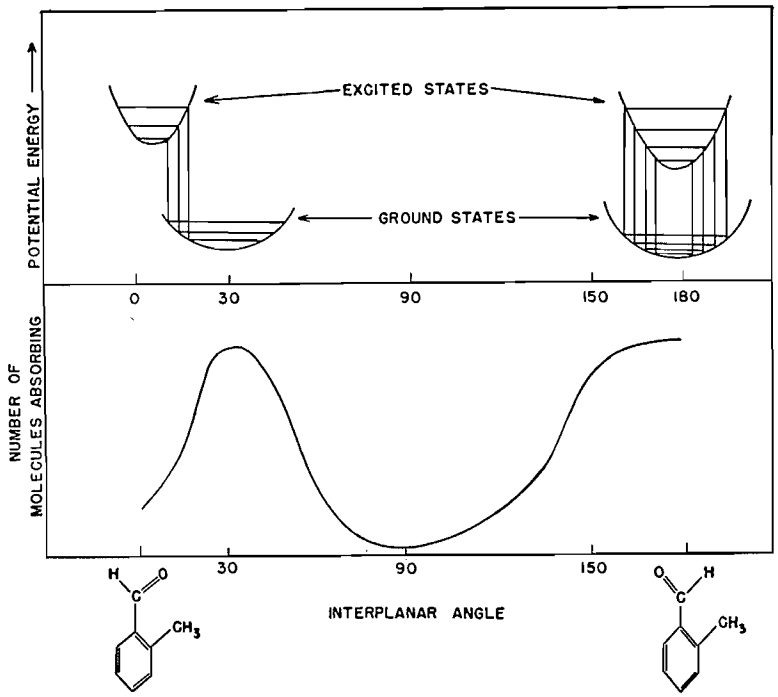

FIG. 2. *Top.*—Schematic representation of electronic transitions between ground and excited states in 2-methylbenzaldehyde.

Bottom.—Distribution curve for ground state molecules of 2-methylbenzaldehyde contributing to the observed absorption.

however, follow from this more detailed treatment thus:

1. The previously noted observation (7) that values of absorption intensities (ϵ) are sometimes halved, when one possible planar form is hindered while the other is not, can be deduced immediately from Equation [1]. This follows since if θ_1 is $\sim 0°$ (i.e. one planar form) and θ_3 is large (i.e. one non-planar form), then $\cos^2\theta_1 \rightarrow 1$ and $\cos^2\theta_3 \rightarrow 0$; hence ϵ/ϵ_0 will tend towards $\frac{1}{2}(1-0) = \frac{1}{2}$, and this therefore explains the observed approximate halving of absorption intensity.

2. Conversely, if an approximately halved intensity of absorption without appreciable change of location of maximal absorption is observed (designated by Braude and co-workers as a "steric effect" of type I and subsequently referred to thus), then this may be taken as an indication that the observed intensity of absorption is due mainly to one of two possible planar forms.

With this observation in mind the spectrum of 1-acetyl-2-methylcyclohexene (II) would appear to be due mostly to the *s-cis* form (IIA) since the intensity of absorption is almost halved relative to that of 1-acetylcyclohexene (III).

Braude and Timmons (6) have recently fully discussed this spectrum as part of their studies on alicyclic ethylenic ketones and on the basis of their equation they have logically concluded that 1-acetyl-2-methylcyclohexene most probably exists with an interplanar angle of about 45° and not chiefly with an interplanar angle of about 180° (*s-cis* form) as suggested by us and

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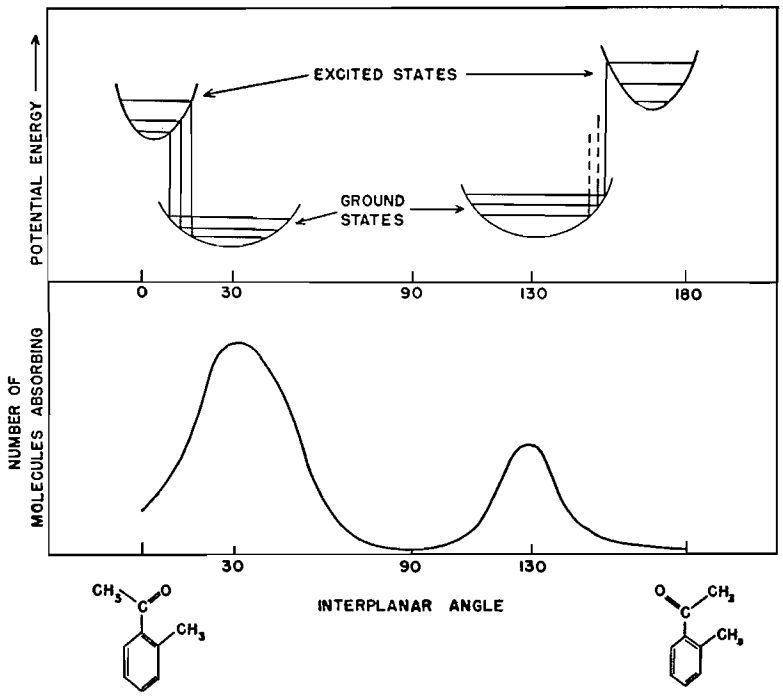
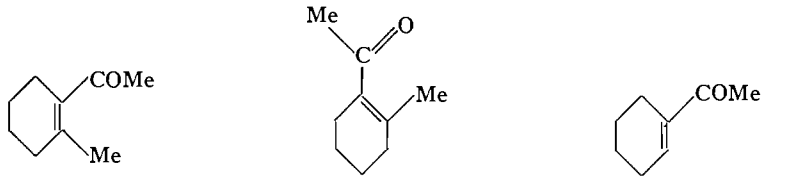


FIG. 3. *Top.*—Schematic representation of electronic transitions between ground and excited states in 2-methylacetophenone.

Bottom.—Distribution curve for ground state molecules of 2-methylacetophenone contributing to the observed absorption.



λ_{max} 245 mμ, ϵ = 6500 — II

IIA

λ_{max} 232 mμ, ϵ = 12,500 — III

also by Turner and Voitle (8). Turner and Voitle conclude that the chromophores in both 1-acetylcyclohexene (III) and 1-acetyl-2-methylcyclohexene (II) are essentially uniplanar, but that whereas the former exists in the *s-trans* conformation, the latter has an *s-cis* conformation. Our interpretation leads us to favor an *s-cis* and *s-trans* conformation for 1-acetylcyclohexene (III) and an *s-cis* conformation only for 1-acetyl-2-methylcyclohexene (II).

This, we suggest, is in fact indicated using the arguments of Braude and Timmons (6) which may be discussed under three headings. The only difference in the treatment is that we shall assume our revised equation, rather than the original equation.

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The first argument of Braude and Timmons assumes as probable that the conformation with $\theta_1 = 45°$ will have a lower potential energy (E_0+1 kcal./mole, where E_0 is the energy of the planar *s-trans* system) than that ($E_0+2.5$ kcal./mole) of the conformation with $\theta_1 = 180°$, and that the former will therefore be preferred. The value of E_0+1 kcal./mole is obtained since no hypsochromic displacement greater than 20 Å, equivalent to about 1 kcal./mole, is observed. Assuming our equation, on the other hand, the absorption intensity due to the conformation with $\theta_1 = 45°$ will contribute only little to the total intensity of absorption and hence a shift of even as much as 60 Å, equivalent to *ca.* 3 kcal./mole, may go unnoticed within the main absorption band due to the conformation with $\theta = 180°$. This then leads to the relations as shown in Fig. 4, where the difference between the curves for any value of θ

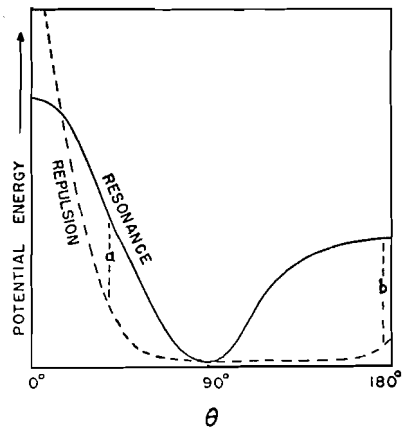

FIG. 4. Dependence of resonance energy and repulsion energy on interplanar angle (schematic). After Braude and Timmons (6).

represents the stabilization energy for that particular conformation. Fig. 4 is so drawn as to show conditions under which this is greater for $\theta = 180°$ (intercept *b*) than for $\theta = 45°$ (intercept *a*).

Braude and Timmons obtain further support for their views by the close agreement between the interplanar angles calculated on the basis of their equation for 1-acetyl-2-methylcyclohexene and 2-methylacetophenone. However, this agreement will equally support our equation, since although the value of 2-methylacetophenone is modified, so is in a similar manner the value for the interplanar angle of 1-acetyl-2-methylcyclohexene.

Finally, support against the *s-cis* conformation is deduced by Braude and Timmons from infrared spectra, since the difference between the ethylenic and carbonyl stretching frequencies is only 57 $cm.^{-1}$, whereas compounds with an enforced *s-cis* configuration consistently give a value of >75 $cm.^{-1}$ for this difference. Although this is clearly an argument against the *s-cis* conformation, we do not consider it a conclusive argument, since the argument does possibly allow for more than one interpretation. For example, 1-acetyl-2-methylcyclohexene will according to our hypothesis exist in the ground state

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in forms which will not contribute to the observed ultraviolet absorption spectrum, but which will presumably contribute to the observed infrared spectrum. As it is, the reported value of 1678 cm.$^{-1}$ for the carbonyl stretching frequency of 1-acetyl-2-methylcyclohexene does not preclude an *s-cis* conformation (cf. 7-Oxoergosta-8(14):22-dien-3-yl acetate, 1680 cm.$^{-1}$ (6), which has a fixed *s-cis* configuration); the value of 1621 cm.$^{-1}$ for the ethylenic stretching frequency does suggest a weaker dipole interaction than is in fact observed for other *cisoid*-systems. However, this weakening may be caused by dipole separation due to steric factors; although precisely what the effect of a slightly sterically hindered molecule is on the ethylenic and carbonyl stretching frequencies does not appear to have been fully worked out.

3. Carrying the argument one step further, one would expect that with three double bonds where four *s-cis* and *s-trans* isomers are possible, it might be possible to obtain steric effects of type I corresponding to a reduction of intensity to approximately 75, 50, and 25%, as the number of permitted planar forms is reduced from four to one.

Fortunately such an example—reasonably closely approximating to the above prediction—appears to be available in the β-ionone series as illustrated in Table II.

As the number of planar *s-cis* and *s-trans* forms is progressively reduced by the introduction of methyl-groups; the intensity of absorption appears to be caused almost exclusively by the remaining planar forms. Thus the location of maximal absorption remains fairly constant, while the absorption intensity is reduced very greatly—roughly proportional to the permitted number of planar *s-cis* and *s-trans* isomers (see Table II).

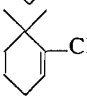
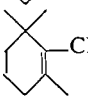
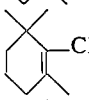
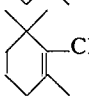
If one were to assume that all the molecules exist in only one *s-cis* or one *s-trans* form while the interplanar angle is progressively increased, a similar ratio of absorption intensities could hardly be accounted for. While the theory of increased interplanar angles, assuming an *s-trans* conformation throughout, could account for the observed changes from (*a*) to (*b*) and from (*d*) to (*e*), it could not easily be invoked to account for the observed intensity changes from (*b*) to (*c*) and from (*c*) to (*d*) which will not affect the interplanar angle of the *s-trans* form (see Table II, Fig. i). A similar argument would also hold if any other conformation were considered to account exclusively for the observed dienone absorption.

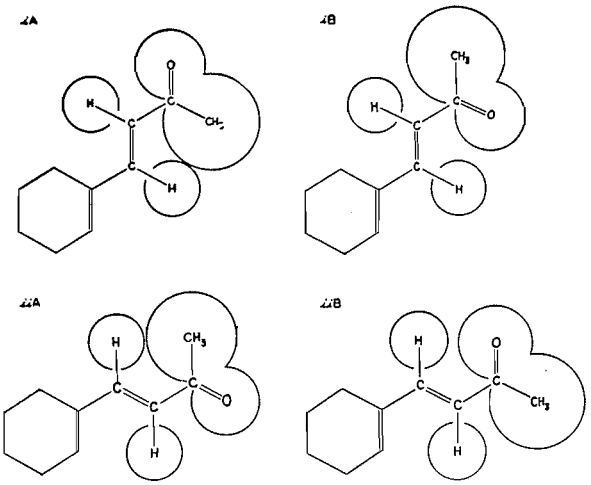
4. The final conclusion which we may draw from the modified equation is, however, probably the most far-reaching. One of the aims of studying the steric effects in ultraviolet light absorption data is to seek an explanation for steric effects of type I as defined previously. One explanation for this phenomenon has been provided by assuming electronic transitions between a non-planar ground state and a near-planar excited electronic state (3, 5).

However, on more closely examining the diagrams either in the above-mentioned paper (3) or in the present communication (see Figs. 1, 2, and 3), it seems likely that as the actual transitions are thus reduced in number, their actual energy values, as estimated from the graph, and even their mean, are no longer identical to the energy values which would represent transitions

TABLE II

ABSORPTION SPECTRA OF β-IONONE AND RELATED COMPOUNDS ACCORDING TO BRAUDE AND JONES (2)

	Compound	Dienone-band λ_{max}, mμ	Dienone-band ϵ_{max}	*s-cis* and *s-trans* isomers (i, ii, iii, iv) contributing to absorption (see figures below)
(*a*)	—CH=CH.COMe	281	20,800	i, ii, iii, iv
(*b*)	 —CH=CH.COMe	281	13,000	ii, iii, i reduced, iv eliminated
(*c*)	 —CH=CH.COMe	296	10,700	ii, i reduced, iii reduced, iv eliminated
(*d*)	 —CH=CH.$COCH_2Me$	295	9400	ii, i reduced, iii further reduced, iv eliminated
(*e*)	 —CH=CMe.COMe	278	4500	ii eliminated, i eliminated, iii and iv as for (*d*)



FIGS. i*A*, i*B* and ii*A*, ii*B* represent the two possible configurations of (i) and (ii). *A* and *B* are not otherwise distinguished, since the —$COCH_3$ group may be considered one unit as a first approximation. (iii) would be as Fig. (ii) except that the —$COCH_3$ group is in the *s-cis* position with respect to the —CH=CH— group. (iv) would be as Fig. (i) except that the —$COCH_3$ group is in the *s-cis* position with respect to the —CH=CH— group, and not in *s-trans* as it is in Fig. (i).

between non-hindered ground and excited states. With this in mind we have somewhat "flattened" our potential energy curves compared to those usually seen in the literature (3, 5) in order to allow for absorption at approximately

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the same maximal wave-length, since the theory as described may not be ruled out completely, but should rather be regarded as an alternative explanation of the observed spectral data.

However, another hypothesis to account for steric effects of type I appears to suggest itself. This is, that steric effects of type I are in fact *only* caused by the number of contributing planar or near-planar *s-cis* and *s-trans* forms being reduced. As soon as only one such *s-cis* or *s-trans* form is possible any further steric hindrance will give rise to a steric effect of type II, namely a shift in the location of maximal absorption, accompanied by reduced absorption intensity.

ACKNOWLEDGMENTS

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NOTES

THE SYNTHESIS OF INDOLE-3-ACETYL-D,L-ASPARTIC ACID AND RELATED COMPOUNDS[1]

By Norman E. Good

It has recently been shown that plants conjugate indole-3-acetic acid with aspartic acid (1, 4). Moreover unpublished work done in this laboratory indicates that the reaction is not confined to indoleacetic acid. Applications of indole-3-propionic acid and indole-3-butyric acid to plants result in the formation of indolepropionylaspartic and indolebutyrylaspartic acids. Consequently it is to be expected that such compounds will continue to interest biochemists and, since their preparation presents certain problems, a generally applicable method of synthesis has been developed. The classical method of amide formation via the acid chloride proved practically useless for derivatives of indoleacetic acid since the conditions necessary for the formation of indoleacetylchloride also led to its rapid decomposition. The mixed anhydride method of Boissonnas (2) which was used successfully in the preparation of other amides of indoleacetic acid (7) was unsatisfactory with aspartic acid, perhaps because of a competing formation of aspartic anhydride. Eventually it was found that esterification of aspartic acid with benzyl alcohol, condensation of the ester with indoleacetic acid through the use of N,N′-dicyclohexylcarbodiimide (6, 5), followed by reductive removal of the benzyl groups resulted in a good yield of indole-3-acetyl-D,L-aspartic acid. The same method when applied to 2,4-dichlorophenoxy-acetic, indole-3-propionic, and indole-3-butyric acids gave comparable yields of the corresponding aspartic derivatives but, unfortunately, neither indolepropionylaspartic acid nor indolebutyrylaspartic acid has been crystallized as yet.

EXPERIMENTAL

Dibenzyl-D,L-aspartate Hydrochloride

The dibenzyl ester of aspartic acid was prepared by a modification of the azeotropic distillation method of Cipera and Nicholls (3). D,L-Aspartic acid (13.3 gm., 0.1 mole) was suspended in 100 ml. of benzyl alcohol (0.97 mole) containing 22.0 gm. benzenesulphonic acid (0.125 mole) in a round-bottomed flask. The flask was warmed for 5–10 min. on a steam bath by which time nearly all of the amino acid had dissolved. Hot carbon tetrachloride (300 ml.) was added and the cloudy reaction mixture was heated until about 10 ml. had distilled off. The flask was then fitted with a Soxhlet extractor containing a thimble filled with anhydrous magnesium sulphate (25 gm.) and the solution heated under reflux overnight. The mixture was allowed to stand at room temperature for several hours. The benzenesulphonic acid salt of dibenzyl-D,L-

[1]*Contribution No. 77, Science Service Laboratory, Canada Department of Agriculture, University Sub Post Office, London, Ontario.*

aspartate was then removed by filtration, washed once with carbon tetrachloride and several times with dry ether. Residual solvent was removed under vacuum. The yield was 40 gm. (85%). (The salt of dibenzyl-L-aspartate is much more soluble in carbon tetrachloride and only precipitates after the addition of a considerable volume of ether.)

The benzenesulphonic acid salt (40 gm.) was suspended in about 300 ml. dry ether and 14 ml. triethylamine was slowly added with stirring. The suspension was allowed to stand for 0.5 hr. with occasional stirring and was then filtered. The precipitate was resuspended in dry ether containing a little triethylamine and the suspension again filtered. Ether and excess triethylamine were removed from the combined filtrates by distillation at reduced pressure and the residue was taken up in 500 ml. dry ether containing 10 ml. benzyl alcohol. Dry HCl was added slowly in considerable excess. The hydrochloride was then removed by filtration and washed with dry ether. The yield was 29 gm. (83% of the aspartic acid).

*Indole-3-acetyl-*D,L*-aspartic Acid*

Dibenzyl-D,L-aspartate hydrochloride (400 mgm., 1.14 mM.) was suspended in tetrahydrofuran (5 ml.), and triethylamine (0.16 ml., 1.14 mM.) was added slowly with stirring. The mixture was allowed to stand for a few minutes after which it was filtered and the precipitate washed with additional tetrahydrofuran. The combined filtrate and washings were then gently heated on a steam bath in a stream of air until nearly all the tetrahydrofuran had been removed. Indole-3-acetic acid (175 mgm., 1.0 mM.) and 1.0 ml. tetrahydrofuran were added. After the indoleacetic acid had dissolved, the viscous solution was cooled somewhat below room temperature and N,N′-dicyclohexylcarbodiimide (220 mgm., 1.05 mM.) in 0.5 ml. tetrahydrofuran was added with vigorous swirling over five minutes. Residual carbodiimide was washed into the reaction mixture with another 0.5 ml. tetrahydrofuran and the stoppered flask was left overnight at room temperature. Ethyl acetate (10 ml.) was added and N,N′-dicyclohexylurea (215 mgm.) was removed by filtration. The filtrate was extracted successively with 0.1 *N* HCl, 0.2 *N* $NaHCO_3$, and water. The solvents were again removed by gently warming in an air stream. The residue was taken up in 50 ml. of *n*-butanol, and palladium catalyst (5% on charcoal) was added. The suspension was shaken under hydrogen (3 atm.) for four hours, whereupon the catalyst was filtered off and washed with more butanol. The filtrate was extracted once with 0.1 *N* HCl, once with water, and three times with 0.5 *N* $NaHCO_3$ (5, 2.5, and 2.5 ml.). The pooled bicarbonate extracts were in turn extracted with ether and the dissolved ether removed by aeration. The aqueous solution was then acidified to pH 2.0 with 80% phosphoric acid. Indole-3-acetyl-D,L-aspartic acid (165 mgm., 57% of the indoleacetic acid) separated as pink crystals when the acidified solution was left overnight in the refrigerator, m.p. 187°–190° C. After treatment with norite and two recrystallizations from water the product was colorless and melted at 190°–191° C. Calc. for $C_{14}H_{14}O_5N_2$: C, 57.9; H, 4.83; N, 9.66. Found: C, 58.1; H, 4.94; N, 9.56%.

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When 2,4-dichlorophenoxyacetic acid was used in place of indole-3-acetic acid a 50% yield of 2,4-dichlorophenoxyacetyl-D,L-aspartic acid resulted. After one recrystallization from 50% alcohol the melting point was 212–214° C. Wood and Fontaine (8) give 217° C. as the melting point of the racemic derivative.

The author wishes to acknowledge the assistance of Mr. R. W. White.

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THE CALCULATION OF THE EXTENT OF ION-PAIR FORMATION IN SOLUTION

BY G. H. DEBUS*

In recent publications (1, 2, 3) extensive use has been made of the Robinson–Stokes equation to evaluate the equivalent conductance of concentrated solutions of strong electrolytes. The agreement between theory and experiment is surprisingly good up to a concentration of about 3 moles per liter.

According to Wishaw and Stokes (6), when the observed conductance is found to be less than the calculated, this must be attributed to ion-pair formation. The results obtained for ammonium nitrate show reasonable constancy of K, the dissociation constant, but the method of Stokes and Wishaw involves laborious calculations; the degrees of dissociation, α, could only be found by a series of approximations and the help of a graph. A graphical and more direct way consists in plotting the experimental and the calculated values (for $\alpha = 1$) of $\kappa\eta/\eta_0$ (product of the specific conductance and the relative viscosity) against the molarity. For equal values of the ordinate the degree of dissociation is obtained by the ratio of the corresponding concentrations.

The mathematical proof of this is as follows: The complete equation for the equivalent conductance, Λ, of a fully dissociated electrolyte is, according to Robinson and Stokes (5):

$$[1] \qquad \frac{1000\kappa}{c} = \Lambda = \left(\Lambda_0 - \frac{B_2\sqrt{c}}{1+B\mathring{a}\sqrt{c}}\right)\left(1 - \frac{B_1\sqrt{c}F}{1+B\mathring{a}\sqrt{c}}\right)\frac{\eta_0}{\eta}.$$

*National Research Council Postdoctorate Fellow at the University of Manitoba, Winnipeg, Manitoba.

When 2,4-dichlorophenoxyacetic acid was used in place of indole-3-acetic acid a 50% yield of 2,4-dichlorophenoxyacetyl-D,L-aspartic acid resulted. After one recrystallization from 50% alcohol the melting point was 212–214° C. Wood and Fontaine (8) give 217° C. as the melting point of the racemic derivative.

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*National Research Council Postdoctorate Fellow at the University of Manitoba, Winnipeg, Manitoba.

At constant temperature, and for a fixed solvent and a fixed electrolyte, å, B, B_1, and B_2 are constant, and F varies only with the concentration, c, i.e.

$$F = \frac{\exp(0.2929B\text{å}\sqrt{c}) - 1}{0.2929B\text{å}\sqrt{c}}.$$

Λ is then only a function of the concentration multiplied by the relative viscosity of the solution:

[2] $$1000\kappa/c = \Lambda = f(c)\eta_0/\eta.$$

For an electrolyte that is not fully dissociated c is substituted by αc and

[3] $$1000\kappa/\alpha c = \Lambda/\alpha = f(\alpha c)\eta_0/\eta.$$

By rearranging, the following is obtained from [2] and [3]:

[4] $$1000\kappa\,\eta/\eta_0 = cf(c) = f^1(c)$$

and

[5] $$1000\kappa\,\eta/\eta_0 = \alpha c\, f(\alpha c) = f^1(\alpha c)\,.$$

The values of $1000\kappa\eta/\eta_0$ for a fully dissociated electrolyte ($\alpha = 1$) are calculated and compared with the experimental values of the weak electrolyte, represented by equation [5].

For each experimental value $\kappa_2\,\eta_2/\eta_0$ of the weak electrolyte, at concentration c_2, there is a corresponding concentration, c_1, of the fully dissociated electrolyte so that (see Fig. 1)

[6] $$1000\kappa_1\,\eta_1/\eta_0 = 1000\kappa_2\,\eta_2/\eta_0$$

and

[7] $$f^1(c_1) = f^1(\alpha c_2)$$

or

$$c_1 = \alpha c_2.$$

The dissociation of the weaker electrolyte at concentration c_2 is equal to c_1/c_2.

A previous method used in this laboratory (3), where α was obtained by the ratio of the experimental value of the equivalent conductance (Λ_2) to the calculated value (Λ_1) at the same concentration, yielded a degree of dissociation which was too high. The deviation increases with the decrease of α.

Indeed, from [2] and [3],

$$\Lambda_1 = f(c)\eta_0/\eta,$$
$$\Lambda_2/\alpha = f(\alpha c)\eta_0/\eta$$

and the concentrations being equal

$$\Lambda_2/\Lambda_1 = \alpha f(\alpha c)/f(c)\,.$$

$f(c)$ decreases with increasing concentration, and consequently at the same concentration $f(\alpha c) > f(c)$, or $\Lambda_2/\Lambda_1 > \alpha$.

The method of equation [5] has been applied to the calculation of the degree of dissociation of the ionization of trichloroacetic acid, a substance which is completely ionized in dilute solution but associates at higher concentration.

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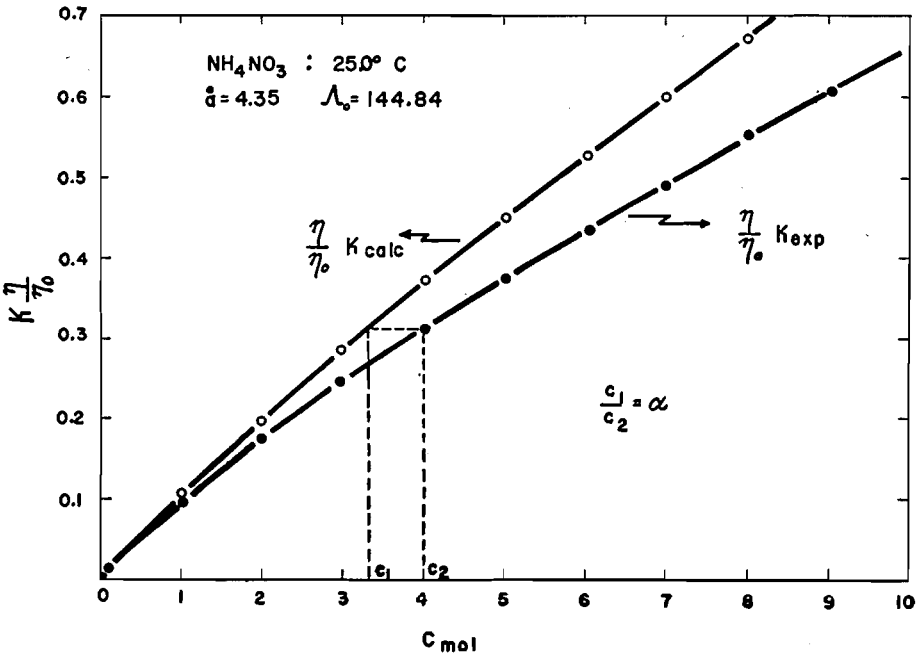

FIG. 1.

The values obtained for the ionization constant (K) showed some variation. This may be explained by the uncertainty in the values of Λ_0, å, γ, and by approximations during calculation and interpolation of experimental values. As mentioned previously a breakdown in the theory is expected at concentration above 3 moles.

RESULTS

The results (4) are contained in Table I.

TABLE I

C_{mol}	Λ_{exp}	Λ_{calc} å = 5.5 Λ_0 = 387.5	$\kappa\eta/\eta_{0exp}$	$\kappa\eta/\eta_{0calc}$	α	K
0.01	—	373.7	—	—	—	—
0.0446	352.7	358.3	0.01601	0.01626	0.983	1.77
0.1010	335.7	341.8	0.03530	0.03600	0.980	3.10
0.1521	323.8	331.2	0.05221	0.05354	0.977	3.78
1.009	207.0	232.2	0.2936	0.3294	0.890	3.56
1.566	156.0	195.9	0.3965	0.4980	0.785	2.24
2.044	121.4	166.3	0.4677	0.6409	0.714	2.65
3.166	67.72	121.3	0.5294	—	0.540	1.01
3.777	46.68	101.0	0.5220	—	0.436	0.82
4.568	28.83	82.3	0.4698	—	0.322	0.63

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THE EFFECT OF ELECTROLYTES ON THE RATE OF CHLORIDE LOSS FROM CHLOROPENTAMMINE CHROMIUM (III) ION IN AQUEOUS SOLUTION

BY M. IKUTA, H. G. MCADIE, and W. MACF. SMITH

We have examined the effect of various electrolytes on the rate of aquation of chloropentammine chromium (III) nitrate,

$$Cr(NH_3)_5\,Cl^{++} + H_2O \rightarrow Cr(NH_3)_5\,H_2O^{+++} + Cl^-,$$

with the view of extending data relating to the specific effects of various ions on the rate of reaction. First order kinetics were established for this reaction by Freundlich and co-workers (4).

The nitrate of chloropentammine chromium (III) was prepared by Christensen's method (3) and on analysis showed contents of chromium and chlorine agreeing with the theoretical to within 1 part in 200. The other salts were of reagent grade. The course of the reaction was followed by determining the amount of free chloride in a 5 ml. aliquot by titration with 0.02 molar (*M*) silver nitrate using a differential titration technique (7) involving two silver electrodes connected to an amplifier based on a design of Lyons and Heller (6). Glass stoppered Pyrex volumetric flasks (100 ml. capacity) served as reaction vessels; they were thermostatted in a Sargent bath covered with a black hood.

Preliminary studies at 30° using a concentration of complex salt of about 0.0085 *M* established that heterogeneous reaction and back reaction were negligible and that satisfactory first order plots involving concentration and time were obtained. It was also found that the addition of the nitrates of potassium, sodium, and calcium to 0.12 *M* concentration increased the first order rate constant by about 10%, that the sulphates of both potassium and sodium at 0.06 *M* concentration increased the rate constant by about 55%, and that the sulphate of magnesium at 0.06 *M* concentration increased the rate constant by about 40%. These observations parallel those of Garrick (5) on the aquation of chloropentammine cobalt (III) ion, which indicated that the influence of the added salt is essentially dependent on the nature and concentration of the anion and that the effect of cation is secondary, probably operating only through its influence on ionic strength and to some degree through its ability to associate with the added anions.

The addition of sodium perchlorate led to a slight drop in rate constant for solutions 0.0065 *M* in complex from 1.13×10^{-3} min.$^{-1}$ in the absence of perchlorate to 1.10×10^{-3} at a perchlorate concentration of 0.10 *M*. Addition

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THE EFFECT OF ELECTROLYTES ON THE RATE OF CHLORIDE LOSS FROM CHLOROPENTAMMINE CHROMIUM (III) ION IN AQUEOUS SOLUTION

BY M. IKUTA, H. G. MCADIE, and W. MACF. SMITH

We have examined the effect of various electrolytes on the rate of aquation of chloropentammine chromium (III) nitrate,

$$Cr(NH_3)_5\,Cl^{++} + H_2O \rightarrow Cr(NH_3)_5\,H_2O^{+++} + Cl^-,$$

with the view of extending data relating to the specific effects of various ions on the rate of reaction. First order kinetics were established for this reaction by Freundlich and co-workers (4).

The nitrate of chloropentammine chromium (III) was prepared by Christensen's method (3) and on analysis showed contents of chromium and chlorine agreeing with the theoretical to within 1 part in 200. The other salts were of reagent grade. The course of the reaction was followed by determining the amount of free chloride in a 5 ml. aliquot by titration with 0.02 molar (*M*) silver nitrate using a differential titration technique (7) involving two silver electrodes connected to an amplifier based on a design of Lyons and Heller (6). Glass stoppered Pyrex volumetric flasks (100 ml. capacity) served as reaction vessels; they were thermostatted in a Sargent bath covered with a black hood.

Preliminary studies at 30° using a concentration of complex salt of about 0.0085 *M* established that heterogeneous reaction and back reaction were negligible and that satisfactory first order plots involving concentration and time were obtained. It was also found that the addition of the nitrates of potassium, sodium, and calcium to 0.12 *M* concentration increased the first order rate constant by about 10%, that the sulphates of both potassium and sodium at 0.06 *M* concentration increased the rate constant by about 55%, and that the sulphate of magnesium at 0.06 *M* concentration increased the rate constant by about 40%. These observations parallel those of Garrick (5) on the aquation of chloropentammine cobalt (III) ion, which indicated that the influence of the added salt is essentially dependent on the nature and concentration of the anion and that the effect of cation is secondary, probably operating only through its influence on ionic strength and to some degree through its ability to associate with the added anions.

The addition of sodium perchlorate led to a slight drop in rate constant for solutions 0.0065 *M* in complex from 1.13×10^{-3} min.$^{-1}$ in the absence of perchlorate to 1.10×10^{-3} at a perchlorate concentration of 0.10 *M*. Addition

of only perchloric acid led to a fairly sharp drop to a rate constant of 1.03×10^{-3} min.$^{-1}$ at an acid concentration of 0.025 *M*. Further increase in acid concentration led to a slight but significant decrease in rate constant almost identical with that produced by addition of sodium perchlorate. Apparently the inhibiting effect of hydrogen ions is substantially absent at concentrations in excess of 0.025 *M* at 30°C.

Further experiments on the effect of added electrolytes involved solutions in which perchloric acid was present in 0.030 *M* concentration and in which one of nitrate, sulphate, iodate, or dichromate of potassium was added to various concentrations. The ionic strength consequently varied. The data are presented graphically in Fig. 1. Some data for the effect of added sodium

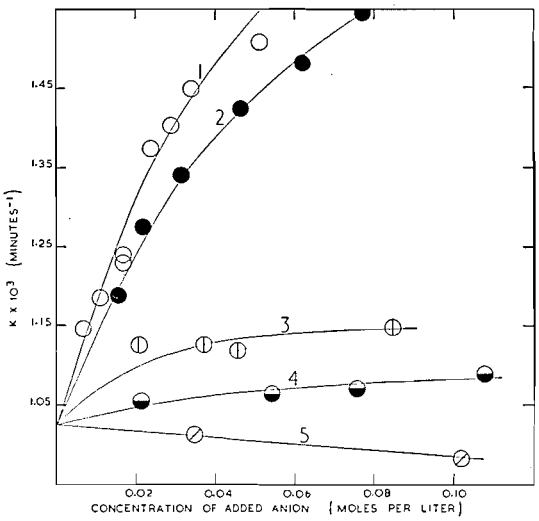

FIG. 1. Effect of added electrolyte on rate constant.

Curve number	Added electrolyte	Curve number	Added electrolyte
1	KIO_3	4	KNO_3
2	K_2SO_4	5	$NaClO_4$
3	$K_2Cr_2O_7$		

All solutions 0.030 *M* in $HClO_4$, 0.0065 *M* in $[Cr(NH_3)_5Cl](NO_3)_2$.

perchlorate are included. The concentrations of nitrate and perchlorate indicated on the figure do not include the contribution of nitrate from $[Cr(NH_3)_5Cl](NO_3)_2$ or of the perchlorate from the perchloric acid. The increases in rate constant accompanying addition of sulphate or nitrate are significantly less than those noted in the experiments in which no perchloric acid was added, e.g. this increase is 45% in the presence of acid compared to nearly 55% in the absence of acid when sulphate was present in a concentration of 0.06 *M*. Some measurements were also made on solutions in which potassium chloride or nitrate was added to various concentrations, perchloric acid was present in 0.030 *M* concentration, and the ionic strength was adjusted to 0.30 with sodium perchlorate. In estimating ionic strength it was assumed that association of sodium or potassium ions with the anions was negligible. The data obtained at constant ionic strength indicated a linear plot of rate

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constant against nitrate concentration with a slope of 6.5×10^{-4} min.$^{-1}$ moles^{-1} liter, and also confirmed that chloride has no significant effect on the rate of aquation up to the maximum concentration of chloride investigated, i.e. 0.10 *M*.

From the data given in Fig. 1 it is apparent that sulphate and iodate are much more effective than dichromate in accelerating the rate of aquation and that nitrate has a small positive, and perchlorate a slight depressive, effect. The predominant species in the solutions to which dichromate, iodate, or sulphate was added are $Cr_2O_7^=$, IO_3^-, and $SO_4^=$ but quantitative interpretation of the data is complicated by the equilibria:

$$\begin{aligned} Cr_2O_7^= + H_2O &\rightleftharpoons 2HCrO_4^-, \\ SO_4^= + H^+ &\rightleftharpoons HSO_4^-, \\ IO_3^- + H^+ &\rightleftharpoons HIO_3. \end{aligned}$$

The latter two equilibria operate to reduce hydrogen ion concentration as well as to depress the concentration of the free anion $SO_4^=$ or IO_3^-. We are deferring quantitative interpretation until we have more information about the separate effectiveness of the various anionic species (e.g. $SO_4^=$ and HSO_4^-) in solution, and the influence of ionic strength on this effectiveness.

It is apparent that the variation in rate constant for the aquation reaction with concentration of added electrolyte is not controlled essentially by ionic strength even at low concentrations but is specifically dependent on the nature of the anion. This observation is in accord with the principle first emphasized by Brönsted (2) that only ions of opposite charge can approach sufficiently closely to permit specific interactions to attain importance. We have been unable to detect removal of iodate or sulphate from solution during progress of the aquation reaction but this does not rule out the possibility that these ions are exerting their influence via a bimolecular replacement of chloride followed by a rapid aquation reaction. It might be expected that the effect of perchlorate would be describable in terms of purely electrostatic influences as in the theory of Bateman *et al.* (1) dealing with the influence of ionic strength on the rate of the unimolecular formation of two ions from a neutral molecule. If this were so, and if the mechanism of chloride ions were indeed unimolecular, an increase in the concentration of sodium perchlorate should lead to an increase in rate constant. In fact there is a slight decrease.

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PREPARATIVE PARTITION CHROMATOGRAPHY OF CARBOHYDRATES ON CELITE COLUMNS[1]

BY R. U. LEMIEUX, C. T. BISHOP, AND G. E. PELLETIER

ABSTRACT

Partition on Celite columns, using both elution and extrusion techniques, was found to be a convenient and satisfactory chromatographic method for preparative or analytical work involving carbohydrates and their derivatives. The method is superior to other chromatographic procedures for carbohydrates in resolution of mixtures; cost, ease, and speed of operation; yield and purity of products; and range of applicability. To illustrate these advantages a number of specific examples are given involving partially methylated derivatives of D-glucose and D-xylose and isolation of products from reaction mixtures.

The use of Celite* to support the static phase in partition chromatography was reported soon after the discovery of this technique (19). This use for the material gained rapid and widespread application in the field of organic chemistry, for example, to resolve fatty acids (24), hydroxy acids (15), fermentation products (22, 23, 25), and alkaloids (2). Although Neish (21, 22, 23) has used silica gel and Celite interchangeably in the separation of such fermentation products as glycerol and 2,3-butanediol, the only other applications made in the field of carbohydrates to our knowledge are those of Baker (12) and of Lemieux and Cipera (16). Our experience in these laboratories has convinced us that columns supported by Celite for partition chromatography provide the most convenient and satisfactory chromatographic method presently available to carbohydrate chemists for preparative and analytical work. This communication describes in some detail the basis for this conclusion.

Mixtures of sugars and their derivatives have been separated by adsorption chromatography using a wide variety of adsorbents, for example, magnesol (18), alumina (11), clays (17), charcoal (26), and silicic acid (10). Certain of these methods possess virtues which ensure their continued use, especially for the separation of such closely related compounds as anomers and certain diastereoisomers. Nevertheless, these methods are subject to the unpredictability of adsorption chromatography and are difficult, expensive, and time-consuming. To avoid these difficulties most workers have favored methods of

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partition chromatography, especially the one in which the static phase is supported by cellulose either in the form of columns (4, 6, 7, 8) or large sheets (3). It is to this method, because of its widespread use and resemblance in applicability, that the use of Celite columns is best compared. The comparison is based on resolution of mixtures; cost, ease, and speed of operation; yield and purity of product; and range of applicability. The Celite technique is believed superior in all respects.

Our experience indicates that the resolving power of Celite columns is at least equal to that of cellulose sheets and better than that of cellulose columns under comparable conditions of operation. The data given in Table I are typical of those which form the basis for this conclusion.

TABLE I

SEPARATION OF D-XYLOSE AND ITS METHYL ETHERS ON A CELITE COLUMN

Fraction number (2 ml. each)	D-Xylose derivative	Yield (mgm.)	$[\alpha]_D^{25}$ (c = 1 in water)	Reported $[\alpha]_D$
70–120	2,3,4-Tri-*O*-methyl	76.9	+19.0°	+18.0°
130–161	2,3-Di-*O*-methyl	67.0	+22.0°	+23.0°
162–191	2,4-Di-*O*-methyl	15.7	+22.0°	+22.0°
250–305	3-*O*-Methyl	51.6	+18.6°	+17.0°
A further 400 ml.	D-Xylose	86.8	+17.3°	+18.8°
Recovery		298.0 (96.1%)		

A measure of the relative mobilities of materials on Celite No. 535 columns is given by the following dimensionless term:

$$R_V = dr^2/V \ (\text{mm.}^3 \times \text{ml.}^{-1}). \quad [1]$$

In this expression d is the distance from the top of the column to the center of the band of material, r is the radius of the column, and V is the volume of developing phase used to obtain the chromatogram. The R_V term is of value because it was found to bear a rough but useful relationship to the R_f term of paper chromatography. For example, using the operating conditions described here and the *n*-butanol: water solvent system, the following relationship held true with useful accuracy (see Fig. 1):

$$R_V = 300\ R_f + 15. \quad [2]$$

It was found empirically that 1 cc. of packed column contains about 0.29 gm. of Celite and that the approximate optimum load for a chromatogram is 10 mgm. of each component per cm.^{2} of column cross-sectional area. We have found it useful to apply this knowledge together with expressions [1] and [2] for predicting the conditions required to obtain a given separation. The approximate relationship between R_V and R_f values has also been used to locate compounds on an extruded Celite column when the compounds were insensitive to the spray reagents that could be used.

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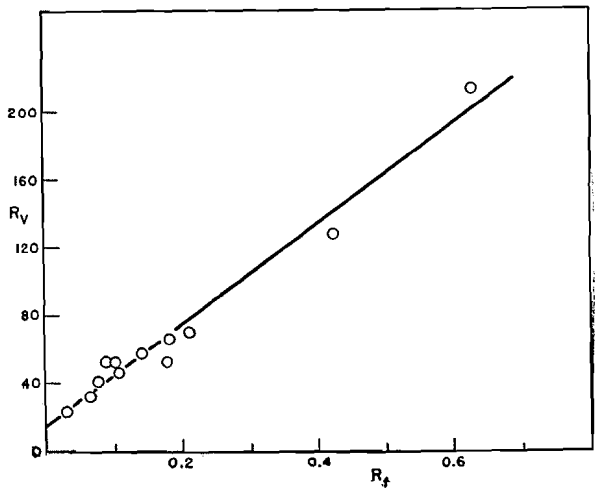

FIG. 1. The relationship obtained between the R_V (Celite column) and R_f (Whatman No. 1 paper) values using the *n*-butanol–water systems in each case.

Celite No. 535 is a low-cost, inert material that can be reclaimed repeatedly; consequently chromatographic separations can be made at a small fraction of the cost of the material and equipment required in using cellulose sheets. Because of its unique physical properties and structure, uniform Celite columns are easily and quickly constructed using the slurry technique (22). With a little practice only 15 to 30 min. are required for the preparation of a column which will extrude easily and perfectly from a tapered tube. In contrast, the construction (7) of cellulose columns is a slow laborious process and the developed columns cannot be extruded. It is important to note in this respect that extrusion chromatography using Celite columns eliminates the need for a fraction collector.

Celite allows ready passage of the developing phase. Primarily because the gravity flow rate through Celite columns is about 10 times that of cellulose columns, separations requiring 12 to 14 days on cellulose columns have been accomplished in only one to two days on Celite columns. The extrusion technique allows the separation of many closely related compounds in only two to three hours and the products are recovered in much more concentrated solution. In comparison, the preparation of preparative paper chromatograms together with location and elution of the separated products is very time-consuming.

Sugars or their derivatives which have been separated by partition on cellulose are always contaminated by material which is often difficult to remove. The impurities are either present in the cellulose to begin with or arise from a slow breakdown of the cellulose under the conditions used. The chemical nature of this material has been studied by Smith *et al.* (9). Although recoveries of sugars from cellulose columns are nearly quantitative, the use of paper sheets can result in severe losses of material. Acid-washed Celite has none of these disadvantages since the chemically inert material is essentially

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non-adsorbing. Minute particles of Celite which sometimes pass into the eluate can be quantitatively removed by filtration through a fine filter such as a bacterial filter plate. The absence of contaminants promises to be of great value in the identification of separated compounds by infrared absorption spectroscopy.

Although we report only the use of the *n*-butanol: water system, a wide variety of solvent systems can be used for partition chromatography on Celite (12, 15, 22, 24) and also a succession of different solvents can be used in the course of a given separation (15, 23). The fact that Celite can be used to support buffered solutions (2) is of practical importance; for example, addition of ammonia to the *n*-butanol: water system was of considerable assistance in separating uronic acids from sugars (1). The method can be used to advantage for removing salts, mineral acids, and mineral bases from carbohydrate materials; for example, D-gulose from its complex with calcium chloride, D-glucose diethyl thioacetal from a mercaptolysis reaction mixture, and D-glucose from a sodium borohydride reduction of D-gluconolactone.

EXPERIMENTAL

The columns are constructed as described in detail by Neish (22). The use of acid-washed Celite No. 535 is recommended because recoveries are improved (22). We found no advantage in drying the material at 500° C. over drying at 110° C. The practice of using a 1:1 volume to weight ratio of stationary phase to Celite provided optimum conditions. The technique of Lemieux and Charanduk (15) is believed most convenient for adding the sample to the top of the column. An approximately 10% solution of the sample (preferably in the developing phase) is absorbed on dry Celite No. 535 (1 ml./gm.) and the resulting powder is packed to the top of a packed Celite column which is just filled with developing phase. The developing phase is then percolated through the column either by gravity or under pressure. The high porosity of Celite columns permits a wide range of flow rates. Our experience indicates that a flow rate of about 0.1 ml./min./cm.^{2} of column cross-sectional area is desirable. However, four to five times this rate can often be used. A sample size of about 10 mgm. of each component per cm.^{2} of column cross-sectional area appears about optimum for preparative work. Of course the width of the band increases as it travels down the column. It is of great practical importance to realize that much larger samples (by a factor as large as 10) can be used when the R_V values of the components differ substantially. For example, 3,5-di-*O*-methyl-D-glucose was separated from about 4% of 3-*O*-methyl-D-glucose by passing 5.4 gm. of the mixture through a 500 gm. Celite column having a radius of 37.5 mm.

The following specific examples were chosen to illustrate the various features of the method.

Separation of Methylated D-*Xyloses*

A mixture (310 mgm.) of *O*-methyl ethers of D-xylose, obtained by hydrolysis of a methylated polysaccharide, was resolved on a Celite column (3.75×34 cm.,

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80.0 gm. Celite) using water-saturated butanol. The eluate was fractionated into 2-ml. portions by an automatic collector which changed the receiver every 72 sec. Distribution of components among the receivers was determined by qualitative paper chromatographic examination of every fifth fraction. Portions of eluate were combined to give solutions of each individual sugar. The solutions were evaporated to dryness and the residues were redissolved in water. These solutions were then clarified by filtration and evaporated to dryness in weighed flasks. Table I shows the results of the separation. The spontaneous crystallization of 2,3,4-tri-*O*-methyl- and 2,4-di-*O*-methyl-D-xylose was a further indication of the purity of the separated components. The remaining fractions were crystallized eventually or yielded crystalline derivatives. After the monomethyl derivative had all been eluted the column was removed from the automatic collector and the eluate was collected in 100-ml. portions until all the D-xylose was removed as shown by a negative test with aniline oxalate spray (5).

Separation of Partially Methylated D-*Glucoses*

(*a*) *Elution*

The hydrolyzate, 300 mgm., of a water-soluble methyl cellulose (13) was resolved into five distinct fractions on a 35 mm. (diam.) column of Celite, 72 gm., as shown by colorimetric assay of successive aliquots of the eluate using the anthrone reagent (20). Inspection of the fractions by paper chromatography showed the first band (200 to 460 ml. of eluate) to be 2,3,6-tri-*O*-methyl-D-glucose (crystallized), the second (490–565 ml.) and third (580–670 ml.) bands to be two different di-*O*-methyl-D-glucoses (one of which crystallized spontaneously from a sirup), the fourth band (930–1320 ml.) to be a mixture of mono-*O*-methyl-D-glucoses, and the fifth band to be D-glucose. This last band was removed from the column by changing the developing phase to water.

(*b*) *Extrusion*

The hydrolyzate, 147 mgm., was chromatographed on a 35 mm. (diam.) column of Celite, 40 gm., using 170 ml. of developing phase. The extruded column was sprayed through a mask (14) with alkaline permanganate (18). The four separate bands which developed were cut out and the contents washed out with water. The materials were shown to be 2,3,6-tri-*O*-methyl-D-glucose (R_V = 228), 41 mgm., a mixture of di-*O*-methyl-D-glucoses (R_V = 122), 38.4 mgm., a mixture of mono-*O*-methyl-D-glucoses (R_V = 69), 42 mgm., and D-glucose (R_V = 39), 15.4 mgm., which was slightly contaminated with mono-*O*-methyl-D-glucoses. The per cent recovery was 92.5.

Separation of Product from Sodium Borohydride Reduction

D-Glucono-δ-lactone (205.7 mgm.) in water (1.3 ml.) at 0° C. was reduced by sodium borohydride (33.0 mgm.) in water (0.7 ml.) according to the method of Wolfrom and Wood (28) for reduction of sugar lactones to aldoses. Excess sodium borohydride was decomposed by addition of 0.5 *N* sulphuric acid and the resulting clear solution (3.5 ml.) was added to dry, acid-washed Celite

(3.5 gm.) which was then placed on the top of a Celite column (80 gm., 38×340 mm.). Water-saturated butanol was passed through the column and the eluate was collected in 7-ml. portions by an automatic fraction collector which changed the receiver every five minutes. Every fifth fraction was tested for aldose content by the aniline oxalate spray reagent (5). Positive tests were given by fractions 225–374 inclusive. These fractions were combined and evaporated to a sirup which was redissolved in water (20 ml.). This solution was passed through a medium porosity sintered glass funnel and the filtrate was evaporated to a colorless sirup which was dried to constant weight over phosphorus pentoxide at 0.02 mm. The product (192 mgm., 92.4%) had $[\alpha]_D^{25} = +48.2°$ ($c = 3.84$ in water) and was crystallized from methanol–isopropyl alcohol to yield α-D-glucose (104 mgm.), m.p. and mixed m.p. 145.5–147° C., $[\alpha]_D^{25} = +76°$ after one-half hour falling to +52.6° in 24 hr. ($c = 1.16$ in water). The mother liquors from this crystallization yielded a further 66 mgm. of the same product.

Mercaptolysis of D-*Glucose*

Wolfrom and Karabinos (27) have shown that diethyl thioacetals are useful derivatives for the characterization of sugars. For this reason and the fact that thioacetals and related compounds have proved extremely valuable in determinations of structures of natural products, it was decided to test the value of the present chromatographic technique for the isolation of the product formed in a mercaptolysis. D-Glucose diethyl thioacetal was readily isolated in an extremely high state of purity from the reaction of micro amounts of glucose with ethyl mercaptan and concentrated hydrochloric acid in the usual manner. The reaction mixture could be added directly to the column or neutralized with sodium carbonate before chromatography. The thioacetal possessed the high R_V value of 254 which rendered its separation from D-glucose extremely easy.

Separation of D-*Glucose,* D-*Fructose, and Sucrose*

A mixture of D-glucose, D-fructose, and sucrose (100 mgm. of each) was dissolved in water (1 ml.), taken up on Celite (1 gm.), and added to the top of a column of Celite (80 gm., 35×380 mm.). The chromatogram was developed with 1500 ml. of water-saturated *n*-butanol and the column was then extruded. The alkaline permanganate spray reagent (18), applied through a mask (14), revealed two bands 260–295 mm. and 320–380 mm. from the top of the column. These two portions of the column were sectioned out and eluted with water. Evaporation of the eluate from the band nearer the top of the column yielded sucrose (81 mgm., 81%), $[\alpha]_D^{29} = +65°\pm2°$ ($c = 1.8\%$ in water). By the same procedure, the band at the bottom of the column yielded D-glucose (100 mgm., 100%), $[\alpha]_D^{29} = +54°\pm2°$ ($c = 2\%$ in water). No other band could be found on the column, so the solvent used to develop the chromatogram was evaporated and yielded D-fructose (74 mgm., 74%), $[\alpha]_D^{29} = -92°\pm1.5°$ ($c = 1.5\%$ in water). The three separated sugars were examined by paper strip chromatography using *n*-butanol saturated with water as the irrigating solvent. Both sucrose and D-fructose were chromatographically

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pure and the D-glucose contained only a slight trace of D-fructose, obviously very little since the specific rotation of the D-glucose was not affected. There is little doubt that D-glucose, D-fructose, and sucrose could be separated completely by using a longer column or the elution technique.

Miscellaneous Experiments

The general usefulness of the technique has been further illustrated by application in these laboratories to the separation of partially esterified sugars, anhydro sugars from their parent compounds, and uronic acids from sugars.

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EFFECTS OF COMPLEXING ON THE HOMOGENEOUS REDUCTION OF MERCURIC SALTS IN AQUEOUS SOLUTION BY MOLECULAR HYDROGEN[1]

By G. J. Korinek[2] and J. Halpern[3]

ABSTRACT

The effects of various complexing agents on the homogeneous reduction of mercuric salts by molecular hydrogen in aqueous solution were determined. In all cases the kinetics suggest that the rate-determining step is a bimolecular reaction between a mercuric ion or complex and a hydrogen molecule, probably leading to the formation of an intermediate mercury atom. The reactivity of various mercuric complexes was found to decrease in the following order: $HgSO_4 > Hg^{++} > HgAc_2$, $HgPr_2 > HgCl_2 > HgBr_2 > Hg(EDA)_2^{++}$. Addition of anions such as OH^-, $CO_3^=$, Ac^-, Pr^-, and Cl^-, in excess of the amounts required to form stable mercuric complexes, was found to increase the rate. An interpretation of these effects is given.

INTRODUCTION

Mercuric salts are reduced homogeneously by molecular hydrogen in aqueous solution to mercurous salts or, under certain conditions, to metallic mercury. A detailed kinetic study of this reaction has been made in the case of mercuric perchlorate (7) and some preliminary results have also been reported for mercuric acetate (4). In view of the marked differences in kinetics which were observed (the rate of reduction of mercuric acetate was much lower than that of the perchlorate) it seemed of interest to study the acetate system in greater detail and also to determine the effects on the reaction of other organic and inorganic complexing agents. The results of these studies are described in the present paper. A related investigation of the effects of complexing on the homogeneous catalytic activation of hydrogen by cupric salts has also been described recently (10).

EXPERIMENTAL

Ethylenediamine (EDA) and ethylenediaminetetraacetic acid (EDTA) were Eastman white label products. The perchlorate salts were obtained from G. F. Smith Chemical Co. All other chemicals were Baker and Adamson reagent grade. Hydrogen and nitrogen gases were supplied by Canadian Liquid Air Co. Distilled water was used in the preparation of all solutions.

The solutions were analyzed for Hg(I) by potentiometric titration with $KMnO_4$. In most cases the total Hg concentration was determined by titration with KCNS using a ferric indicator, following acidification and oxidation with $KMnO_4$ where necessary. With solutions containing chloride or bromide, Hg(II) determinations were made by the iodide method (6). An excess of KI

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(beyond that necessary to convert all the Hg(II) to the stable $HgI_4^=$ complex) was added, and back-titrated with $HgCl_2$ to the first appearance of a red precipitate of HgI_2.

The experiments were conducted in a stainless steel autoclave which has been described previously (2). When corrosive solutions (such as those containing chloride or bromide) were used, a titanium liner was placed in the autoclave and the stainless steel stirrer, thermocouple well, and sampling tube were replaced by titanium counterparts. Three liters of solution, of desired composition, was placed in the autoclave, which was then sealed, flushed with nitrogen, and heated to the desired reaction temperature, maintained to within ± 0.3°C. throughout the experiment with a Micromax recording controller. In each experiment, it was ascertained that the solutions were stable at the reaction temperature in the absence of hydrogen. Where any reduction of Hg(II) (i.e. as a result of side reactions with the metal autoclave or with organic complexing agents) was detected, its rate was determined and subtracted from the subsequently measured rate of reduction in the presence of hydrogen. It can be seen from the rate plots that this correction was generally small. After the hydrogen was introduced (taken as zero reaction time) its partial pressure above the solution was held constant throughout the experiment. To follow the reaction, the solution was sampled periodically and analyzed for Hg(I) and Hg(II) as described earlier.

The concentration of hydrogen in solution, $[H_2]$, was estimated from the measured partial pressure using available data for the solubility of H_2 in water (11, 13). It was ascertained that the stirring (provided by an impeller of 2.5 in. diameter, rotating at 950 r.p.m.) was adequate to keep the solution saturated with hydrogen throughout the reaction.

RESULTS AND DISCUSSION

It is convenient to divide the systems studied into three categories depending on whether the reduction product is (i) a soluble mercurous salt, (ii) an insoluble mercurous salt, or (iii) metallic mercury. Each of these categories is characterized by different stoichiometric and kinetic patterns which are described in Table I.

Reactions in the first category are distinguished by the fact that H_2 is activated by interaction, not only with the mercuric salt but also with the mercurous ions which result from its reduction. The resulting kinetics, and the methods used to evaluate the rate constants k_1 and k_2, have been described in connection with an earlier study of the reduction of mercuric perchlorate (7).

In the reactions of the other two categories, only the mercuric salts contribute to the activation of H_2, in each case apparently through a bimolecular rate-determining step (characterized by the rate constant k_1) involving a dissolved mercuric ion or complex and an H_2 molecule. Since the concentration of H_2 is kept constant throughout the reaction, the resulting kinetics are of first order (i.e. in the Hg(II) concentration).

Values of k_1 were estimated from the slopes of linear kinetic plots, using the appropriate rate equations. In order to facilitate kinetic comparison of different

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TABLE I

CLASSIFICATION OF REACTIONS

	Category		
	I	II	III
Systems	Perchlorate, nitrate, sulphate	Acetate,* propionate,* chloride, bromide	EDA and EDTA complexes in basic soln.
Reaction stoichiometry	$2Hg(II) + H_2 \rightarrow 2Hg(I)$ (soluble)	$2Hg(II) + H_2 \rightarrow 2Hg(I)$ (ppt.)	$Hg(II) + H_2 \rightarrow Hg$
Rate-determining steps	$Hg(II) + H_2 \xrightarrow{k_1}$ $Hg(I)_2 + H_2 \xrightarrow{k_2}$	$Hg(II) + H_2 \xrightarrow{k_1}$	$Hg(II) + H_2 \xrightarrow{k_1}$
Rate law	$-d[Hg(II)]/dt = 2k_1[Hg(II)][H_2] + k_2[Hg(I)][H_2]$	$-d[Hg(II)]/dt = 2k_1[Hg(II)][H_2]$	$-d[Hg(II)]/dt = k_1[Hg(II)][H_2]$
Integrated rate equation	$\log\left(\frac{2k_1/(2k_1 - k_2)\ [Hg(II)]_0}{[Hg(II)] + [k_2/(2k_1 - k_2)][Hg(II)]_0}\right) = \frac{(2k_1 - k_2)[H_2]t}{2.3}$†	$\log\frac{[Hg(II)]_0}{[Hg(II)]} = \frac{2k_1[H_2]t}{2.3}$	$\log\frac{[Hg(II)]_0}{[Hg(II)]} = \frac{k_1[H_2]t}{2.3}$

Although mercurous acetate and propionate are appreciably soluble, they do not contribute to the activation of H_2. Hence the kinetics conform to those of category II.

†*This equation is derived in Ref. 7.*

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systems (since the activation of H_2 is rate-limiting in all cases) the rate laws defining k_1 are uniformly expressed in terms of the equivalent rate of reaction of H_2 ($-d[H_2]/dt$). The latter could be calculated from the measured rate of reduction of Hg(II) and the known stoichiometry of the reaction. All forms of Hg(II) were found to contribute to the activation of H_2, although with varying rates. Hence with solutions containing more than one mercuric species the apparent value of k_1, determined in this way, obviously represents a weighted average of the rate constants for all the species present.

The investigations of the individual systems, the results of which are described below, generally involved the determination of (i) the products and stoichiometry of the reaction, (ii) the kinetic dependence on the Hg(II) and H_2 concentrations, and (iii) the effects of varying the solution composition, pH, concentrations of complexing agents, etc.

Nitrate

The kinetics of the reduction of Hg(II) to Hg(I) in nitrate solution were found to be identical with those for perchlorate (7). The rate was unaffected by variations in solution composition, in the range 0.05–0.75 *M* HNO_3 and 0–1 *M* $NaNO_3$. The extent of complexing in this system (i.e. between Hg^{++} and NO_3^-) is apparently slight (5) and, as in the perchlorate system, H_2 is activated by interaction with simple Hg^{++} and Hg_2^{++} ions. At 86°, the measured value of k_1, 0.397 liter mole^{-1} sec.$^{-1}$, was in good agreement with that determined earlier for perchlorate solutions (7).

Sulphate

Although the form of the kinetics remained substantially unchanged, the addition of sodium sulphate to a solution of mercuric perchlorate was found to increase the rate of reduction of Hg(II) to Hg(I) (reflected in an increased value of k_1) as shown in Figs. 1 and 2. This is attributed* to complexing

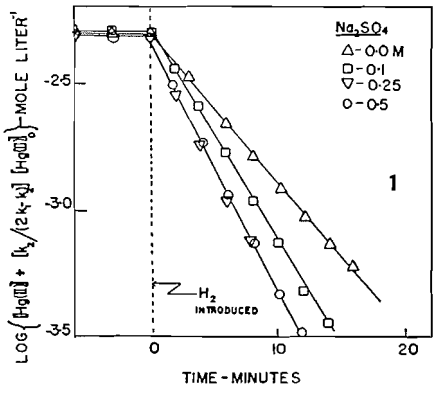

FIG. 1. Rate plots showing the effect of sulphate on the reduction of Hg(II) at 86°, 4 atm. H_2, in solutions containing initially 0.005 *M* $Hg(ClO_4)_2$, 0.02 *M* $HClO_4$.

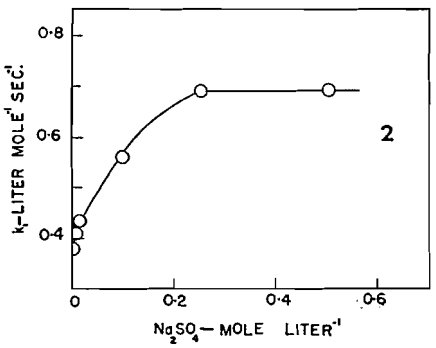

FIG. 2. Effect of sulphate on k_1 (same conditions as in Fig. 1).

**Since the addition of sodium perchlorate was always found to be without effect on the rate, it seems reasonable to attribute the effects obtained with other sodium salts to the respective anions.*

between Hg^{++} and $SO_4^{=}$ (5) and, by analogy with similar observations in the cupric system (10), it seems reasonable to conclude that the constant value of k_1 (0.69 liter mole^{-1} sec.$^{-1}$ at 86°), attained at $SO_4^{=}$ concentrations above 0.25 *M*, represents the rate constant for the activation of H_2 by the undissociated $HgSO_4$ molecules. Its reactivity is about 80% higher than that of the uncomplexed Hg^{++} ion.

Acetate

A preliminary study of the reduction of mercuric acetate by hydrogen was described earlier (4). The product of the reaction is mercurous acetate, which has only a limited solubility (ranging from 0.003 *M* at room temperature to about 0.04 *M* at 100°) and starts to precipitate from the solution before the reaction is complete.

Some rate plots depicting the reduction of mercuric acetate are shown in Fig. 3. As in the perchlorate system, the reaction is characterized by two

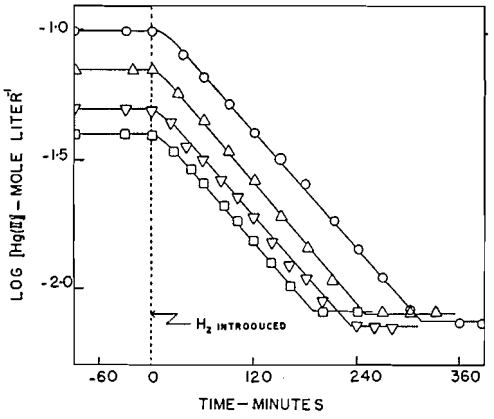

FIG. 3. Rate plots for the reduction of mercuric acetate at 90.2°, 4 atm. H_2.

distinct kinetic regions. The initial first order region (the rate here is also first order in H_2) corresponds to the reduction of Hg(II) to Hg(I), referred to earlier. As this reaction proceeds, the Hg(II)—Hg(I) potential is lowered (as a result of the decreasing Hg(II) concentration) and ultimately reaches the point where the reduction of Hg(I) to metallic Hg becomes preferred thermodynamically. The horizontal portion of the rate plot apparently represents a region in which only the latter reaction is occurring. The concentration of Hg(I) retains a constant value in this region (determined by the solubility of mercurous acetate) and hence no further Hg(II) reacts until all the precipitated mercurous acetate has been reduced to metallic mercury. Consistent with this interpretation, it was found that the limiting Hg(II) concentration ($\approx$0.007 *M* at 90°) is essentially independent of the initial Hg(II) concentration and of the H_2 partial pressure, but that it increases slightly with the temperature (presumably reflecting the increasing solubility of mercurous acetate). Although its solubility at the reaction temperatures is appreciable,

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it seems fairly clear from the kinetics that the mercurous acetate product (in contrast to the uncomplexed Hg_2^{++} ion (7)) does not contribute significantly to the activation of H_2 in this system.

Rate measurements over the temperature range 69° to 115° yielded a good Arrhenius plot, which is fitted by the equation: $k_1 = 1.3\times10^{10} \exp[-19{,}400/RT]$ liter mole^{-1} sec.$^{-1}$. The activation energy is about 1300 cal./mole higher than that for mercuric perchlorate (consistent with the lower rate) and the frequency factor is normal for a simple bimolecular reaction in solution. It seems likely that the above expression for k_1 represents the rate constant for the bimolecular activation of H_2 by the $HgAc_2$ molecule, the extent of whose dissociation in aqueous solution is known to be small (8). At 90.2°, the value of k_1 (0.02 liter mole^{-1} sec.$^{-1}$) is about 25 times smaller than that for the uncomplexed Hg^{++} ion. This is in marked contrast to the results reported for the activation of H_2 by cupric salts, where the acetate complex is about 120 times more reactive than the simple Cu^{++} ion (9).

Addition of sodium acetate to a solution of mercuric acetate was found to increase the rate as shown in Fig. 4. The increase is linear in the acetate concentration and may reflect the formation of higher mercuric acetate complexes such as $HgAc_3^-$ and $HgAc_4^=$ which are more reactive than $HgAc_2$, or alternatively it may be a purely kinetic effect, the possible significance of which will be discussed later.

Propionate

The results of a few experiments on the reduction of Hg(II) in propionate solution were analogous to those for the acetate system. The reduction product is a precipitate of mercurous propionate. At 90.2°, the value of k_1 (0.021 liter mole^{-1} sec.$^{-1}$) is close to that for mercurous acetate. The linear increase in the rate with increasing sodium propionate concentration (Fig. 4), although slightly greater, parallels the effect observed in the acetate system.

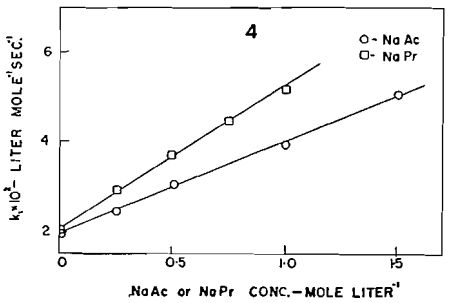

FIG. 4. Effect of excess acetate and propionate, respectively, on the rates of reduction of mercuric acetate and propionate at 90.2°.

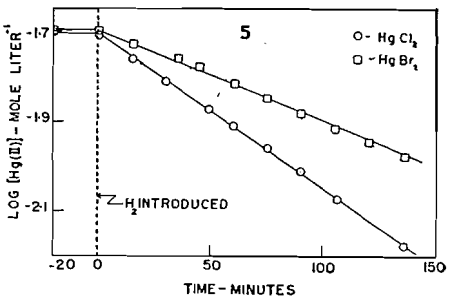

FIG. 5. Rate plots for the reduction of mercuric chloride and mercuric bromide at 123°, 10 atm. H_2.

Chloride

In chloride-containing solutions, the reduction of Hg(II) yields a precipitate of mercurous chloride, whose solubility is negligible. When the ratio of the

initial concentration of Cl^- to that of Hg(II) in the solution was 2 or greater, the kinetics of the reaction were consistently first order in Hg(II) (see Fig. 5) and in H_2. At 123° and a Cl^- to Hg(II) ratio of 2, k_1 was found to have a value of 0.0075 liter mole^{-1} sec.$^{-1}$. Since complexing in this system is probably complete (12), this presumably represents the rate constant for the bimolecular reaction between H_2 and the $HgCl_2$ molecule and is about 400 times smaller than the corresponding value for the uncomplexed Hg^{++} ion.

With further addition of sodium chloride the rate increased slightly (see Fig. 6) approaching a constant value for ratios of Cl^- to Hg(II) greater than about 4.5. The value of k_1 in this region, which presumably represents the rate constant for the reaction of H_2 with $HgCl_4^{=}$, is about 30% higher than for $HgCl_2$.

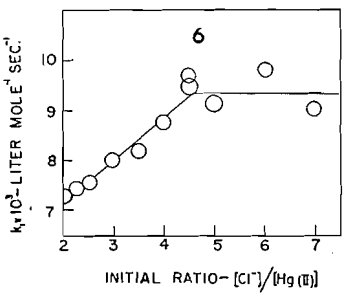

FIG. 6. Effect of excess chloride concentration on the rate of reduction of mercuric chloride at 123°. Initial $HgCl_2$ concentration, 0.02 *M*.

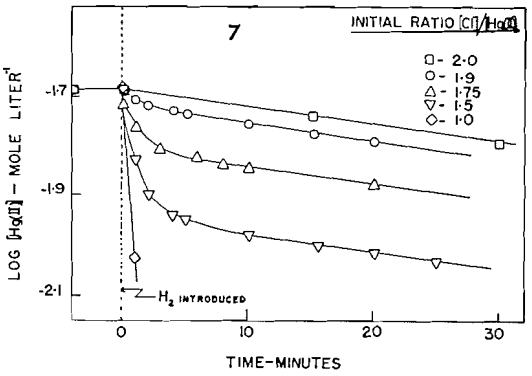

FIG. 7. Rate plots for the reduction of Hg(II) in solutions with various initial Cl^-/Hg(II) ratios at 123°, 10 atm. H_2.

With initial Cl^- to Hg(II) ratios below 2, the kinetics were more complicated, as shown by the rate plots in Fig. 7. The high initial rate is presumably due to the reaction of H_2 with incompletely complexed Hg(II) species such as Hg^{++} and $HgCl^+$. As the reaction proceeds, the ratio of Cl^- to Hg(II) in the solution increases until it reaches a value of 2. Beyond this point, the first order rate plots are, as expected, linear and parallel.

Bromide

The results in bromide-containing solutions parallel those for the chloride system. Hg(II) is reduced to an insoluble precipitate of mercurous bromide. The value of k_1 for $HgBr_2$ (0.005 liter mole^{-1} sec.$^{-1}$ at 123°) is about 30% lower than that for $HgCl_2$.

Ethylenediamine

The effect of EDA on the reduction of Hg(II) was examined in basic solutions where the $Hg(EDA)_2^{++}$ complex is stable. Mercurous salts disproportionate under these conditions so that metallic mercury is the only product of the reaction. The rate of reduction was found to be first order in Hg(II)

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(see Fig. 8), first order in H_2, and independent of the ratio of EDA to Hg(II) in the solution, provided the latter exceeds 2. At 123° and low OH^- concentrations, k_1 was found to be about 0.003 liter $mole^{-1}$ $sec.^{-1}$. It seems reasonable to conclude that this value (which is about 1000 times smaller than that for the Hg^{++} ion) represents the rate constant for the bimolecular reaction between H_2 and $Hg(EDA)_2^{++}$.

It was found, even when an excess of EDA was present, that the rate increased on the addition to the solution of salts of certain anions such as OH^-, Ac^-, Pr^-, and $CO_3^=$, as shown in Figs. 8 and 9. The effects resemble those

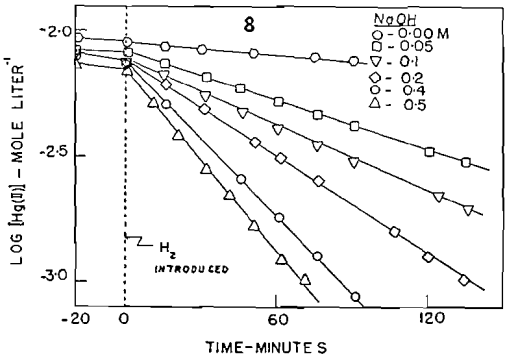

FIG. 8. Rate plots for the reduction of Hg(II) at 123°, 5 atm. H_2, in solutions containing initially 0.01 *M* $Hg(ClO_4)_2$, 0.05 *M* EDA, and various concentrations of NaOH.

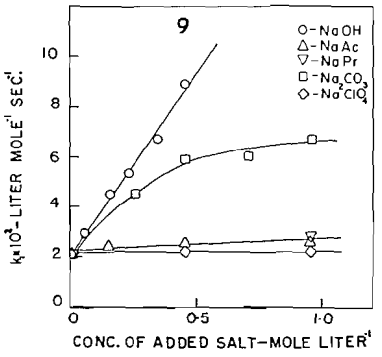

FIG. 9. Effect of various added bases and salts on the rate of reduction of Hg(II) at 123°, in solutions containing initially 0.01 *M* $Hg(ClO_4)_2$, 0.05 *M* EDA, and 0.05 *M* NaOH (in addition to concentration of NaOH or salt shown).

which were observed in the acetate, chloride, and propionate systems on increasing the concentration of the anion (X^-) beyond that required to convert all the Hg(II) to the stable complex HgX_2. In those systems the increased rate seemed attributable to the formation of higher complexes, i.e. HgX_3^- and $HgX_4^=$. However such an interpretation does not fit the present case, since the solution already contains an excess of EDA and all the Hg(II) is presumably present as the very stable $Hg(EDA)_2^{++}$ complex. Further complexing with anions such as OH^-, $CO_3^=$, or Ac^- (except possibly for the formation of weak ionic complexes of the type $Hg(EDA)_2X^+$) seems unlikely, and it is more probable that the increase in rate, caused by these anions, is due to a kinetic effect.

Ethylenediaminetetraacetic Acid

A few experiments were made under similar conditions to those above, using EDTA instead of EDA to complex the Hg^{++}. The resulting rate of reaction between Hg(II) and H_2 could not be measured accurately (because of the competing reduction of Hg(II) by EDTA) but was apparently of the same order as that of the EDA complex.

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CONCLUSIONS

The data obtained in these studies have been used to compile Table II, in which the various mercuric complexes, for which values of k_1 have been determined, are arranged in order of decreasing reactivity toward H_2 (that of the uncomplexed Hg^{++} ion being taken as unity). In each case the probable formula of the reactive complex and its stability constant (where known) are given. The listed values of the relative reactivities are only approximate since they are based on rate measurements at different temperatures (ranging from 90° to 123°) and of varying precision.

TABLE II

RELATIVE REACTIVITIES AND STABILITY CONSTANTS OF VARIOUS MERCURIC COMPLEXES

Complex	Stability constant*	Reactivity†
$HgSO_4$	22 (5)	1.8
Hg^{++}		1
$HgAc_2$	2.7×10^{8} (8)	4×10^{-2}
$HgPr_2$		4×10^{-2}
$HgCl_2$	1.7×10^{13}(12)	2.5×10^{-3}
$HgBr_2$	1.2×10^{15}(12)	1.7×10^{-3}
$Hg(EDA)_2^{++}$	2.6×10^{23} (1)	1×10^{-3}

**Equilibrium constant at 25° for the reaction:* $Hg^{++} + nA \rightleftharpoons Hg(II).A_n$ *(concentrations expressed in mole liter*$^{-1}$*).*

†Value of k_1 *relative to that for* Hg^{++}.

In the case of the simple Hg^{++} ion, it has been proposed, on the basis of kinetic and energetic considerations (3, 7), that the reaction proceeds through the following mechanism, involving the intermediate formation of a free Hg° atom, i.e.

$$Hg^{++} + H_2 \xrightarrow{k_1} Hg^{\circ} + 2H^{+} \text{ (slow)}, \qquad [1]$$

$$Hg^{\circ} + Hg^{++} \rightarrow Hg_2^{++} \text{ (fast)}. \qquad [2]$$

In view of their similar kinetic pattern, it seems likely that the other mercuric complexes react by the same mechanism. Since the rate-determining step presumably involves the transfer of electrons from H_2 to Hg(II), it would be expected to be influenced by the following considerations:

1. The unfilled low-lying electronic orbitals of Hg^{++}, on which this electron transfer depends, may be used up to varying degrees in forming covalent bonds with complexing ligands, with a resulting decrease in the electron affinity of the Hg(II) species and, hence, in its reactivity toward H_2. The inverse correlation, apparent in Table II, between the stability of the complexes and their reactivity, is consistent with this interpretation. The $HgSO_4$ complex, which is more reactive than the simple Hg^{++} ion, is relatively unstable and is probably of the ionic type. This is also the case for the various cupric complexes (e.g. $CuSO_4$, $CuAc_2$, $CuPr_2$, $CuCl_4^{=}$) whose reactivities toward H_2 are greater than that of the simple Cu^{++} ion and which are also much less stable than the corresponding mercuric complexes (10).

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2. Apart from the above consideration, the reaction should be favored by the presence of reagents of high basicity, capable of stabilizing the H^+ ions which are released in the rate-determining step. It is probable that this explains the general promoting influence of basic anions on the reaction under conditions such that Hg(II) is already complexed to the point where any additional reduction of its electron affinity, through further complexing, is unlikely. This is probably the case for the chloride, acetate, and propionate systems, when the ratio of the concentration of complexing anion to that of Hg(II) is greater than 2, and for the EDA system where the promoting influence on the reaction of various anions was found to follow the same order as their basicities, i.e. $OH^- > CO_3^= > Pr^-$, $Ac^- > ClO_4^-$. To be effective in this way, the anion may participate in the reaction either as a separate kinetic entity or by complexing with Hg(II). In the former case, the rate would increase linearly with the anion concentration, while in the latter case a saturation effect might be expected. Both types of behavior have been observed.

An alternative interpretation, not readily distinguishable from that just given, has been proposed to explain the catalytic influence which certain anions (e.g. OH^- and Cl^-) exert in other electron transfer reactions such as the exchange between isotopic metal ions of different valence. It has been suggested that the anion forms a polarizable bridge between the two reacting species, thereby lowering the electrostatic repulsion barrier to their mutual approach and facilitating electron transfer between them (14). It is possible that some of the anion influences observed in the present reaction should also be regarded in this light.

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THE INFRARED ABSORPTION SPECTRA OF DEUTERATED ESTERS

I. METHYL ACETATE[1]

By B. Nolin[2] and R. Norman Jones

ABSTRACT

By comparison of the infrared absorption spectrum of methyl acetate with the spectra of three deuterium substitution products, it has been possible to assign the bands in the 3100–2800 cm.$^{-1}$ and 1500–1300 cm.$^{-1}$ regions of methyl acetate to vibrations localized in the individual methyl groups. Bands characteristic of the individual trideuteromethyl groups are also identified between 2300 and 2000 cm.$^{-1}$. The C=O stretching frequency is observed to shift to lower frequency with increasing deuteration. The spectra in the range 1300–700 cm.$^{-1}$ are also reported.

INTRODUCTION

The use of deuterium substitution as an aid in the interpretation of the infrared spectra of organic compounds of low symmetry has been demonstrated in previous publications from this laboratory (4, 6, 9). In an endeavor to gain more information concerning the nature of the absorption bands characteristic of alkyl esters, a series of deuterated analogues of methyl acetate and ethyl acetate have been synthesized, and their infrared spectra compared. This paper is concerned only with the spectra of methyl acetate (I) and the three deuterated analogues II–IV; the ethyl acetate spectra will be dealt with separately (10). More recently, deuterated analogues of methyl laurate have been synthesized by Dr. L. C. Leitch and their spectra will be discussed in a later publication.

I. $CH_3.CO.O.CH_3$

II. $CD_3.CO.O.CH_3$

III. $CH_3.CO.O.CD_3$

IV. $CD_3.CO.O.CD_3$

EXPERIMENTAL

The preparation and chemical and physical characterization of the deuterium substituted methyl acetates have been described elsewhere (8). Their isotopic purity was at least 99.0 at. % deuterium. The spectra were measured quantitatively in carbon tetrachloride solution between 4000 and 1300 cm.$^{-1}$ and in carbon disulphide solution below 1300 cm.$^{-1}$. A Perkin-Elmer Model 12C single-beam spectrometer was employed with a full range of prisms. A control solvent spectrum was recorded on each chart and duplicate determinations were made for each compound. The absorption intensities were computed

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and plotted as apparent molecular extinction coefficients (7, pp. 276, 287).[3] The computed spectral slit widths (7, p. 274) were approximately 3 cm.$^{-1}$ between 3200 and 2800 cm.$^{-1}$ (with LiF prism); 2 cm.$^{-1}$ between 2400 and 2000 cm.$^{-1}$ (with LiF prism); 3 cm.$^{-1}$ between 1800 and 1300 cm.$^{-1}$ (with CaF_2 prism); and 4 cm.$^{-1}$ at 1300 cm.$^{-1}$ diminishing to 3 cm.$^{-1}$ at 750 cm.$^{-1}$ (with NaCl prism).

RESULTS AND DISCUSSION

It is observed that several of the bands present in the spectrum of the normal compound disappear on deuteration. The missing bands are associated with vibrations localized in the groups which have been deuterated; by inference the bands that remain unchanged on deuteration are attributed to vibrations centered in other parts of the molecule. The absorption spectrum of the fully deuterated analogue IV has also been described by Corval and Lecomte (1), but the infrared spectra of the partly deuterated analogues have not been previously investigated. Our analyses of the spectra of the light and fully deuterated compounds are summarized in Table I, and the individual bands in all the analogues are considered separately below.

TABLE I

GROUP FREQUENCY ASSIGNMENTS IN $CH_3.CO.O.CH_3$ AND $CD_3.CO.O.CD_3$

ν_{max}, cm.$^{-1}$	Group	Type of vibration
	$CH_3.CO.O.CH_3$	
3460	$\rangle C{=}O$	Overtone of carbonyl stretching vibration
3026, 2999	$-O.CH_3$	Combination bands
2957	$-O.CH_3$	Asymmetrical C—H stretching vibration
2905	$-O.CH_3$	Combination band
2846	$-O.CH_3$	Symmetrical C—H stretching vibration
2080	Skeletal	Overtone of 1047 cm.$^{-1}$ band
1748	$\rangle C{=}O$	Carbonyl stretching vibration
1487, 1480	—	
1456	$-O.CH_3$	Asymmetrical C—H bending vibration
1435	$-O.CH_3$	Symmetrical C—H bending vibration
(1401)*	—	See footnote *
1369	$CH_3.CO-$	Symmetrical C—H bending vibration
1312	—	—
1279	—	Methyl bending vibration (?)
1243	Skeletal	See text
1047	Skeletal	See text
980	—	Methyl bending vibration (?)
844	Skeletal (?)	See text

[3] *The apparent molecular extinction coefficient* ($\epsilon_\nu^{(a)}$) *at the wave number* ν *is given by the expression:*

$$\epsilon_\nu^{(a)} = (1/cl) \log_{10}(T_0/T)_\nu$$

where c *is the concentration of the solute in moles per liter of solution,* l *the cell length in cm., and* $\log_{10}(T_0/T)_\nu$ *the apparent optical density when the spectrometer is set to the wave number* ν.

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TABLE I (*Concluded*)

ν_{max}, cm.$^{-1}$	Group	Type of vibration
	$CD_3.CO.O.CD_3$	
3460	$\diagdown$C=O	Overtone of carbonyl stretching vibration
2272, 2254	—O.CD_3	Combination bands
2196	—O.CD_3	Asymmetrical C—D stretching vibration
2128	—O.CD_3	Combination band
2082	—O.CD_3	Symmetrical C—D stretching vibration
2016	—	Combination band
1740	$\diagdown$C=O	Carbonyl stretching vibration
1275	Skeletal	See text
1190	CD_3.CO—	—
1092	Skeletal	See text
1053	—	—
1034†	—	—
970	CD_3.CO— (?)	—
920	CD_3.CO— (?)	—
744	Skeletal (?)	—

**This band is observed in $CH_3.CO.O.CD_3$ but not in $CH_3.CO.O.CH_3$ where it may be overlapped by the much stronger absorption at 1435 cm.$^{-1}$. The bands at 1430 and 1401 cm.$^{-1}$ are alternatives for the asymmetrical C—H bending vibration in the $CH_3.CO$— group; the 1430 cm.$^{-1}$ assignment is supported by comparison with the spectrum of $CH_3.CO.O.CD_2.CD_3$ (10).*

†*Inflection.*

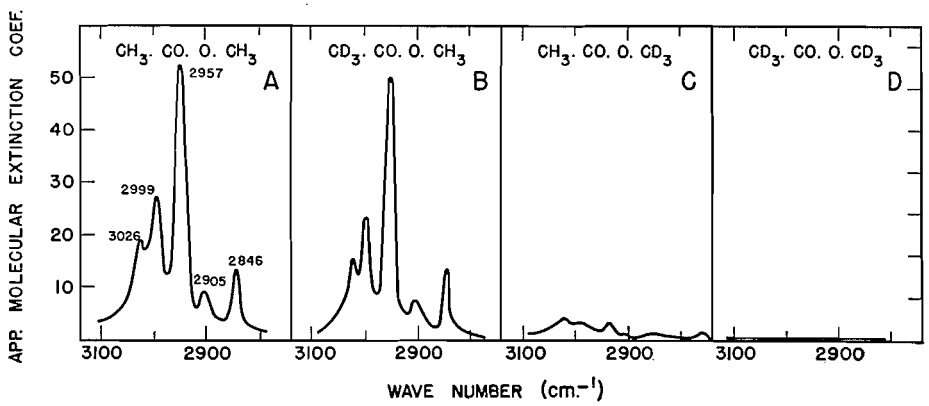

FIG. 1. Infrared spectra. Region of C—H stretching vibrations. (Carbon tetrachloride solution.)

C—H Stretching Vibrations (3050–2800 cm.$^{-1}$)

In methyl acetate (I) we observe bands at 3026, 2999, 2957, 2905, and 2846 cm.$^{-1}$ (Fig. 1A). This spectrum is almost identical with that recorded by Francis (3) who noted the same five maxima. He employed a high resolution grating spectrometer and the extinction coefficients of the two most prominent bands, after interpolation from his curve and conversion to our intensity units, were 42 and 26 respectively (cf. our values of 52 and 26 respectively).

The association of all five of these bands with C—H vibrations is sub-

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stantiated by the fact that they are all absent from the spectrum of the fully deuterated analogue (IV), which shows no measurable absorption in this region of the spectrum (Fig. 1D). Under the experimental conditions employed any bands with $\epsilon_{max}^{(a)} > 0.5$ would have been detected.

The spectra of the partly deuterated analogues II and III are shown in Figs. 1B and 1C. They are of unusual interest, as they demonstrate that the significant absorption of the non-deuterated compound in this region of the spectrum is all associated with the ester methoxyl group, since the spectrum of II is almost identical with that of I, whereas in the spectrum of III the C—H stretching bands are weaker by a factor of 10. This spectrum is reproduced in Fig. 2 with an expanded ordinate scale. This observation conforms with

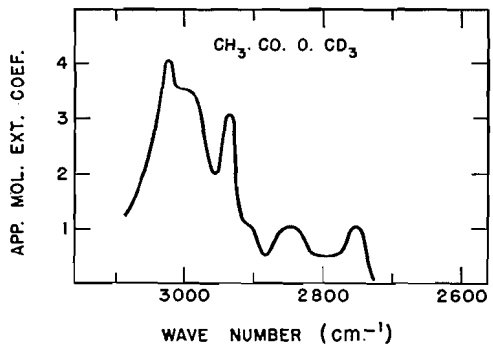

FIG. 2. Infrared spectrum of $CH_3.CO.O.CD_3$ in same spectral region as Fig. 1, but with 10-fold expansion of intensity scale. (Carbon tetrachloride solution.)

Francis's conclusion (3) that the integrated absorption intensity in this region of the spectrum associated with the —$CO.OCH_3$ group is much greater than that associated with the $CH_3.CO.O$— structure. It is also consistent with the behavior of the C—D stretching bands of these compounds (see below) and with our observations on deuterated ethyl acetates (10).

Vibrational theory allows for only two fundamental C—H stretching vibrations for an isolated methyl group. Comparison with the spectra of *n*-paraffin hydrocarbons (7, pp. 339–342) suggests that the bands at 2957 and 2846 $cm.^{-1}$ are probably to be assigned respectively to the asymmetrical and symmetrical C—H stretching vibrations of the ester methoxyl group, and the other three bands to combination tones associated with the same structure.

All our samples of methyl and ethyl acetates, both deuterated and non-deuterated, exhibited a weak band near 3460 $cm.^{-1}$ ($\epsilon_{max}^{(a)}$ 3–5) which was noted also by Corval and Lecomte (1). These authors attributed this band to a trace of methanol impurity, but it is more probably an overtone of the C=O stretching vibration, the fundamental of which occurs near 1745 $cm.^{-1}$.

Between 2800 and 2300 $cm.^{-1}$ weak bands ($\epsilon_{max}^{(a)} < 2$), probably due to overtones, are noted as follows: $CH_3.CO.O.CH_3$ (2595, 2475 $cm.^{-1}$); $CD_3.CO.O.CH_3$ (2605, 2510 $cm.^{-1}$); $CH_3.CO.O.CD_3$ (2755, 2515 $cm.^{-1}$); $CD_3.CO.O.CD_3$ (2565 $cm.^{-1}$).

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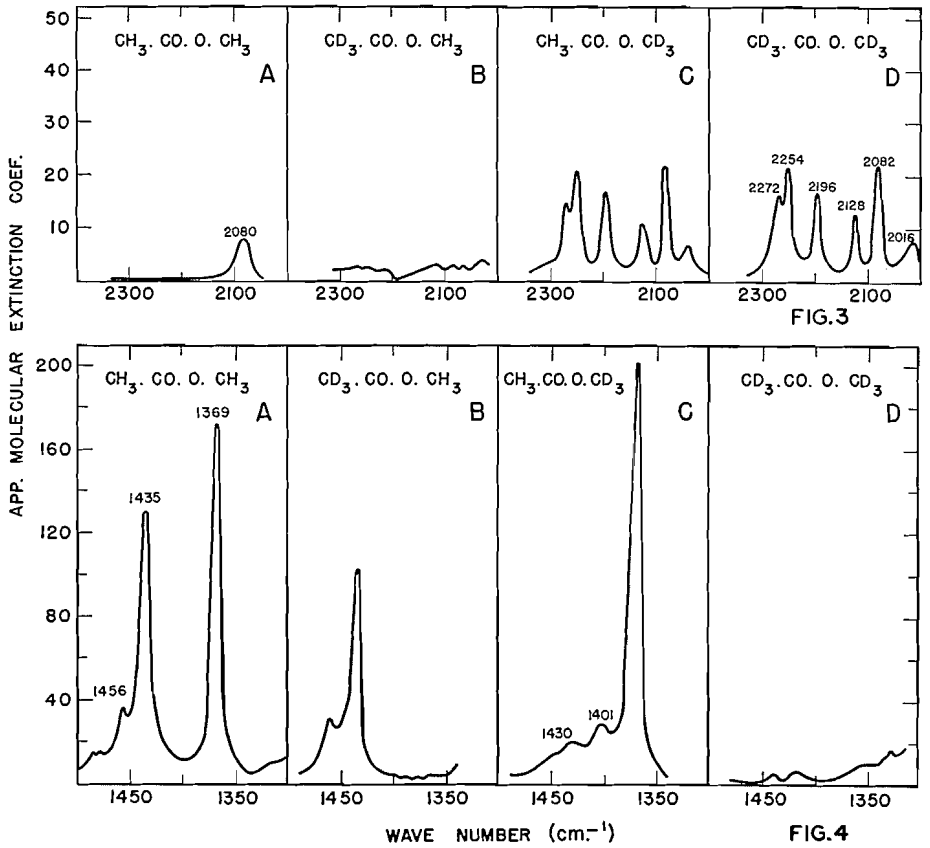

FIG. 3. (Upper figure) Infrared spectra. Region of C—D stretching vibrations. (Carbon tetrachloride solution.)

FIG. 4. (Lower figure) Infrared spectra. Region of the most characteristic C—H deformation vibrations. (Carbon tetrachloride solution.)

C—D Stretching Vibrations (2300–2050 cm.$^{-1}$)

Methyl acetate (I) exhibits a single weak band in this region at 2080 cm.$^{-1}$ ($\epsilon^{(a)}_{max}$ 7) (Fig. 3A). This is possibly an overtone of the strong band at 1047 cm.$^{-1}$ (Fig. 5A). The fully deuterated analogue gives bands at 2272, 2254, 2196, 2128, 2082, and 2016 cm.$^{-1}$ (Fig. 3D). Five of these are probably analogues of the C—H vibrations described above and the sixth may be an overtone of the strong skeletal vibration at 1093 cm.$^{-1}$ by analogy with the 2080 cm.$^{-1}$ of methyl acetate. As the spectra of $CH_3.CO.O.CD_3$ and $CD_3.CO.O.CD_3$ are almost identical in this region (Figs. 3C, 3D) it is evident that only the $—O.CD_3$ trideuteromethyl group is involved in this absorption. Comparison with Figs. 1A and 1B would suggest that the bands at 2196 and 2082 cm.$^{-1}$ may be asymmetrical and symmetrical C—D stretching vibrations of the trideuteromethoxy group, and the remaining bands combination tones. However the relative intensities of these bands do not correspond with those of the analogous C—H absorption; there may be mixing of the vibrations and a redistribution of intensity through coupling with the overtone of the skeletal band near 1090 cm.$^{-1}$.

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Carbonyl Stretching Vibrations (1748–1740 cm.$^{-1}$)

The carbonyl stretching vibration of methyl acetate in carbon tetrachloride solution occurs at 1748 cm.$^{-1}$. The position of the band in the various deuterated esters is given in Table II, from which it will be seen that there is a progressive shift to lower frequency with increasing deuteration, amounting to 8 cm.$^{-1}$ for the fully exchanged compound. Both of the trideuteromethyl groups contribute about equally to the shift and their effect is cumulative. This is similar to the deuteration displacements on the C=O frequency in diethyl ketone (9) and would seem to be a simple mass effect (7, p. 473).

C—H Bending Vibrations (1490–1300 cm.$^{-1}$)

Methyl acetate exhibits prominent bands at 1456, 1435, and 1369 cm.$^{-1}$ and two much weaker bands at 1487 and 1480 cm.$^{-1}$ (Fig. 4A). Francis observed the same spectrum (3); his molecular extinction coefficients for the two principal peaks, as interpolated from his curve, are 165 and 123 in our units, and these compare well with our values of 174 and 130 units.

In compounds of this type it is reasonable to assume *a priori* that the more prominent bands in this region of the spectrum involve C—H deformation vibrations; this is confirmed by the fact that the spectrum of the fully deuterated compound shows negligible absorption (Fig. 4D). Comparison with the spectra of the partly deuterated compounds shown in Figs. 4B and 4C shows clearly that both the 1456 and the 1435 cm.$^{-1}$ bands involve vibrations of the ester methoxyl group, while the 1369 cm.$^{-1}$ band is associated with the ester acetoxy group. This is consistent with earlier observations on more complex acetates and trideuteroacetates from which absorption near 1365 cm.$^{-1}$ was attributed to the acetate methyl group (4). The weak 1430 cm.$^{-1}$ band of $CH_3.CO.O.CD_3$ could also be present in the spectrum of the light ester where it would be obscured by the much stronger 1435 cm.$^{-1}$ band.

From vibration theory we would expect altogether four C—H deformation vibrations associated with each isolated methyl group, and two of these would normally be observed in this region; the others (methyl "rocking" vibrations) occur at lower frequencies. In the *n*-paraffin hydrocarbons the asymmetrical and symmetrical methyl bending vibrations occur at 1460 and 1379 cm.$^{-1}$ (7, pp. 347–349). In methyl acetate we may tentatively assign the bands at 1456 and 1436 cm.$^{-1}$ respectively to the asymmetrical and symmetrical C—H bending vibrations of the ester methoxy group. The 1369 cm.$^{-1}$ band is almost certainly associated with the symmetrical C—H bending vibration of the acetoxy methyl group. Doubt remains as to the assignment of the asymmetrical C—H bending vibration of the acetoxy methyl; this could be one of the weak bands at 1430 or 1401 cm.$^{-1}$ observed only in $CH_3.CO.O.CD_3$; comparison with the spectrum of the ethyl acetate derivatives (10) would suggest that the 1430 cm.$^{-1}$ band is more likely, as a band is also observed at 1430 cm.$^{-1}$ in $CH_3.CO.O.CD_2.CD_3$.

It is also to be noted that whereas the intensities of the C—H stretching bands of the acetoxy methyl group are depressed by the vicinal carbonyl group, the symmetrical C—H bending band at 1369 cm.$^{-1}$ is much intensified. The maximal extinction coefficient of this band in methyl acetate is 174, while

TABLE II

DISPLACEMENT OF C=O STRETCHING AND SKELETAL FREQUENCIES WITH DEUTERATION

	C=O stretching bands,* cm.$^{-1}$	Skeletal bands,† cm.$^{-1}$	
$CH_3.CO.O.CH_3$	1748	1243	1047
$CD_3.CO.O.CH_3$	1743	1256	1077
$CH_3.CO.O.CD_3$	1744	1264	1089
$CD_3.CO.O.CD_3$	1740	1275	1092

Carbon tetrachloride solution.
†*Carbon disulphide solution.*

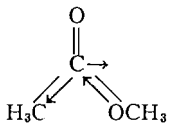
in short chain *n*-paraffin hydrocarbons values of about 20 per methyl group are observed (7, pp. 347–349). This agrees with the conclusions of Francis (3) based on integrated absorption intensity measurements.

Absorption Below 1300 cm.$^{-1}$

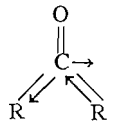
The absorption of the four compounds in the 1300–700 cm.$^{-1}$ region is shown in Figs. 5A–5D. In these spectra we can observe changes characteristic of the deuteration of the specific methyl groups, but we cannot at present assign these to vibrational modes.

In methyl acetate (I) there are two prominent bands, at 1243 cm.$^{-1}$ and 1046 cm.$^{-1}$, which are observed also in more complex acetates (5). Bands clearly corresponding with these are seen in the spectra of the deuterated methyl acetates and they shift progressively to higher frequency with increasing deuteration, as is shown in Table II. In more complex acetates (5) it has been shown that displacement of the 1243 cm.$^{-1}$ band to higher frequency is associated with a lowering of the C=O stretching frequency, and this is seen to hold true also in the deuterated methyl acetates.

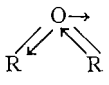
The 1243 cm.$^{-1}$ band in methyl acetate has been identified with the skeletal vibration V (3) by analogy with VI which is a normal mode of vibration in aliphatic ketones. Aliphatic ethers also possess a strong band between 1150 and 1070 cm.$^{-1}$ associated with the asymmetrical stretching vibration VII, and it is possible that the 1243 and 1047 cm.$^{-1}$ bands of methyl acetate result from coupling of V and VII.



V



VI



VII

The band at 844 cm.$^{-1}$ in methyl acetate is strong enough to suggest a skeletal motion involving the significant participation of at least one of the more polar atoms, presumably the carbonyl carbon atom or the methoxy oxygen atom. In the vapor phase spectrum of dimethyl ether there is a band at 940 cm.$^{-1}$ assigned to the symmetrical motion VIII, which might couple

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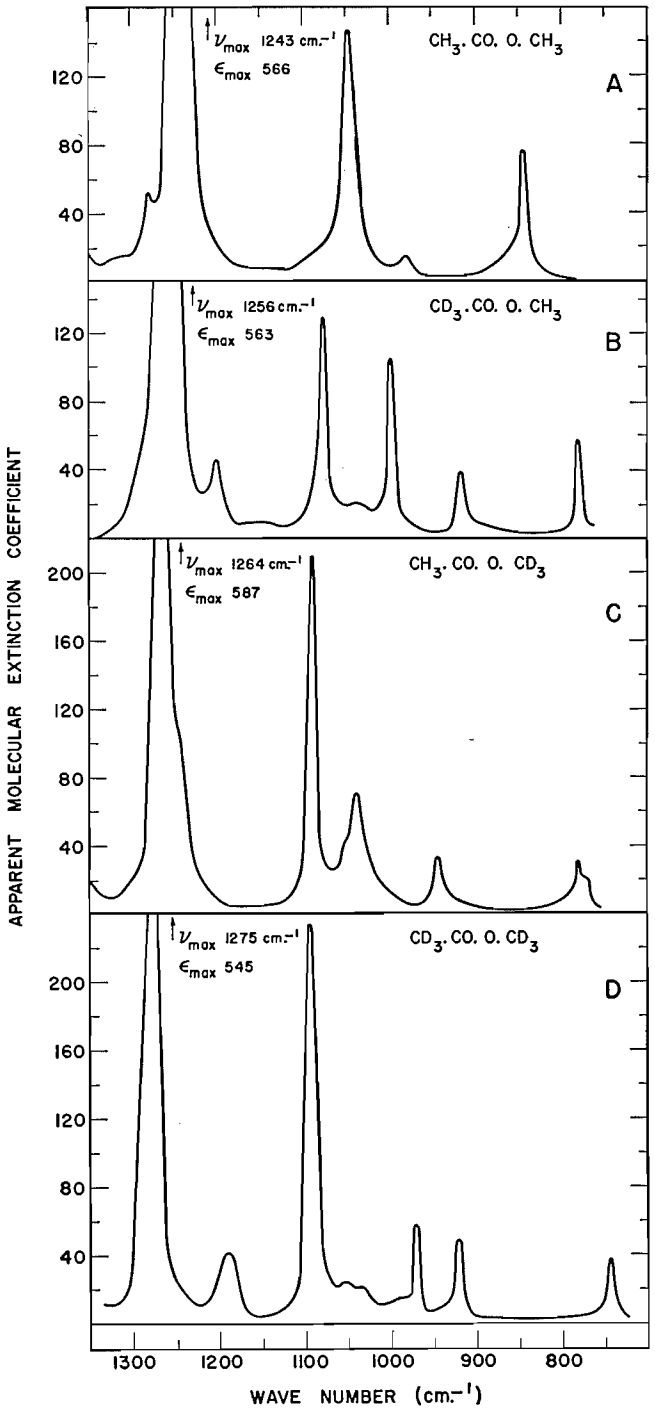
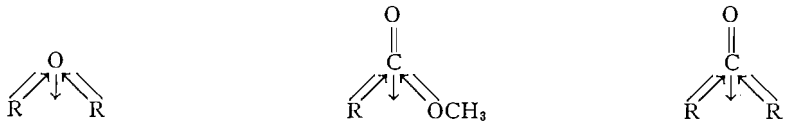


FIG. 5. Infrared spectra. "Fingerprint region". (Carbon disulphide solution.)

with a symmetrical motion IX of the acetoxy group. Vibration IX would be an analogue of the ketone vibration X which is assigned to a band at 790 cm.$^{-1}$ in the infrared spectrum of acetone. In the spectra of the deuterated methyl



VIII IX X

acetates (Figs. 5B–5D) this band is either lost, or displaced into the 780–730 cm.$^{-1}$ range. The weak bands in the methyl acetate spectrum at 1279 and 980 cm.$^{-1}$ may be combination tones or methyl rocking vibrations.

In the deuterated compounds additional absorption will be introduced from the C—D deformation vibrations of the trideuteromethyl groups. In $CD_3.CO.O.CH_3$ bands appear at 1200 cm.$^{-1}$, 998 cm.$^{-1}$, and 916 cm.$^{-1}$ which may correspond with bands at 1192, 970, and 920 cm.$^{-1}$ in $CD_3.CO.O.CD_3$. These can be assigned tentatively to motions localized in the $CD_3.CO$— group and one of the lower two may be the symmetrical C—D bending vibration displaced from 1368 cm.$^{-1}$ in the hydrogen compound. The 998 and 970 cm.$^{-1}$ bands would fit better for a calculated frequency shift by a factor of $1/\sqrt{2}$, but a larger displacement could occur if appreciable mixing with other vibrations is involved.

Characteristic structure appears in the spectrum of $CH_3.CO.O.CD_3$ at 1038 and 944 cm.$^{-1}$ but analogous bands are not recognizable in the spectrum of the fully deuterated compound. All the deuterated compounds show at least one band between 780 and 740 cm.$^{-1}$ which may be the analogue of the 844 cm.$^{-1}$ band of methyl acetate discussed above.

CONCLUDING REMARKS

These comparative studies demonstrate that at frequencies above 1300 cm.$^{-1}$ all the major absorption bands of methyl acetate can be treated in good approximation as associated with vibrations localized within the $CH_3.CO$—, —O—CH_3, or $\diagdown$C=O$\diagup$ groups. They also serve to emphasize the complexity of the C—H stretching absorption. The simple nature of the spectra of aliphatic and alicyclic hydrocarbons between 3100 and 2800 cm.$^{-1}$, which was first demonstrated by Fox and Martin (2), suggested that this region of the spectrum might prove to be very helpful for the interpretation of the molecular structure of more complex compounds. These observations on methyl acetate substantiate the conclusions of Francis (3) and of Pozefsky and Coggeshall (11), as well as earlier work from this laboratory (9), in showing that the C—H stretching absorption is particularly sensitive to the introduction of heteroatoms, in respect to both the band intensities and the prevalence of strong combination bands.

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THE INFRARED ABSORPTION SPECTRA OF DEUTERATED ESTERS

II. ETHYL ACETATE[1]

By B. Nolin[2] and R. Norman Jones

ABSTRACT

The infrared absorption spectrum of ethyl acetate has been compared with the spectra of seven derivatives deuterated in the methyl and methylene groups. In the region 3500–1300 cm.$^{-1}$ most of the bands can be assigned to vibrations localized in the individual groups. Absorption characteristic of the trideuteromethyl and dideuteromethylene groups can be recognized between 2300 and 2000 cm.$^{-1}$. The C=O stretching vibration shows progressive displacement to lower frequency with increasing deuteration. The spectra in the range 1300–700 cm.$^{-1}$ are also reported.

INTRODUCTION

This paper is concerned with a comparison of the infrared spectra of ethyl acetate (I) and seven derivatives (II–VIII) in which deuterium has been introduced selectively into the methyl and methylene groups. This investigation parallels studies of diethyl ketone (4) and methyl acetate (5) which have been reported elsewhere.

I. $CH_3.CO.O.CH_2.CH_3$
II. $CH_3.CO.O.CD_2.CH_3$
III. $CH_3.CO.O.CH_2.CD_3$
IV. $CD_3.CO.O.CH_2.CH_3$
V. $CH_3.CO.O.CD_2.CD_3$
VI. $CD_3.CO.O.CD_2.CH_3$
VII. $CD_3.CO.O.CH_2.CD_3$
VIII. $CD_3.CO.O.CD_2.CD_3$

The preparation of the deuterated esters and their physical and chemical characterization have been described previously (3). In all compounds the isotopic purity was of the order of 99.0 at. % deuterium. These spectra were measured under the same conditions as were the methyl acetate spectra (5).

RESULTS AND DISCUSSION

C—H Stretching Vibrations (3000–2850 cm.$^{-1}$)

The spectra are shown in Figs. 1A–1H. Light ethyl acetate (I) exhibits four distinct bands at 2982, 2939, 2906, and 2873 cm.$^{-1}$ with an additional inflection at 2962 cm.$^{-1}$ (Fig. 1A).

These bands are all associated with C—H vibrations, as the spectrum of

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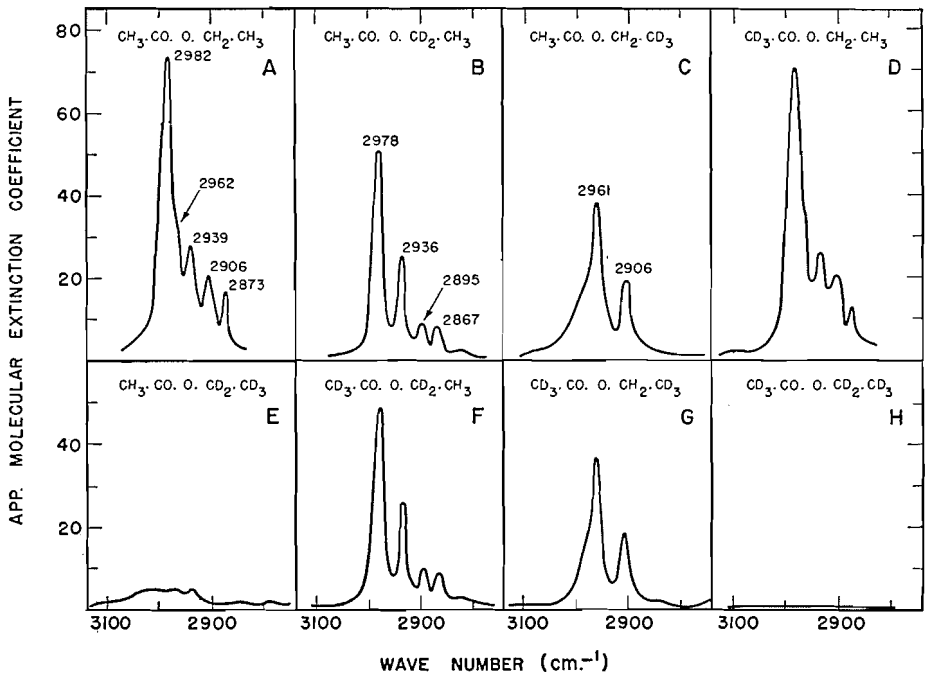

FIG. 1. Infrared spectra. Region of C—H stretching vibrations. (Carbon tetrachloride solution.)

the fully deuterated compound (VIII) shows no absorption in this region (Fig. 1H). The significant absorption is further restricted to the $—CH_2.CH_3$ group, as the spectrum of $CH_3.CO.O.CD_2.CD_3$ is extremely weak (Fig. 1E). Conversely the spectrum of $CD_3.CO.O.CH_2.CH_3$ in this region (Fig. 1D) resembles that of the non-deuterated compound. The weak band system in $CH_3.CO.O.CD_2.CD_3$ is shown more clearly in Fig. 2, where the ordinate scale

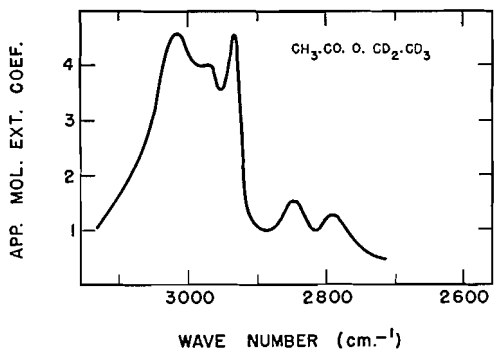

FIG. 2. Infrared spectrum of $CH_3.CO.O.CD_2.CD_3$ in same spectral region as Fig. 1, but with 10-fold expansion of intensity scale. (Carbon tetrachloride solution.)

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is expanded by a factor of 10. Although weak, this absorption would appear to be characteristic for the $CH_3.CO.O$—structure, and closely resembles that observed in the spectrum of the related deuterated methyl acetate ($CH_3.CO.O.CD_3$) shown in Fig. 2 of Reference 5.

A more detailed comparison among these spectra suggests that some of the observed bands are composite; the bands are considered individually below and the tentative assignments for the light and the fully deuterated compounds are summarized in Table I.

TABLE I

GROUP FREQUENCY ASSIGNMENTS IN $CH_3.CO.O.CH_2.CH_3$ AND $CD_3.CO.O.CD_2.CD_3$

ν_{max}, cm.$^{-1}$	Group	Type of vibration
	A. $CH_3.CO.O.CH_2.CH_3$	
3460	$>C=O$	Overtone of carbonyl stretching vibration
2982	$-CH_2-CH_3$	Asymmetrical C—H stretching vibration of methyl group superimposed on weak methylene absorption
2962*	$-CH_2-$	Asymmetrical C—H stretching vibration
2939	$-CH_3$ of ethoxy group	Combination band (see 2873 cm.$^{-1}$ band)
2906	$-CH_2-CH_3$	Primarily a symmetrical C—H stretching vibration of the methylene group superimposed on weaker methyl absorption
2873	$-CH_3$ of ethoxy group	Symmetrical C—H stretching vibration (this might be reversed with the 2939 cm.$^{-1}$ band)
1741	$>C=O$	Carbonyl stretching vibration
1475	$-CH_2-CH_3$	See text
1464	$-CH_2-CH_3$	An overlapping doublet, one component of which is probably the scissoring C—H deformation vibration of the methylene group
1446	$-CH_3$ of ethoxy group	Asymmetrical C—H bending vibration
1430*	CH_3-CO-	Asymmetrical C—H bending vibration
1393	$-CH_2.CH_3$	Principally a symmetrical C—H bending vibration of the methyl group, perturbed from 1380 cm.$^{-1}$ by interaction with a methylene vibration and further displaced by interaction with the 1373 cm.$^{-1}$ vibration of the acetoxy methyl group (cf. 1359 cm.$^{-1}$ band)
1373	$CH_3.CO-$	Symmetrical C—H bending vibration
1359	$-CH_2.CH_3$	Principally a (wagging?) vibration of the methylene group, perturbed from 1382 cm.$^{-1}$ by interaction with a methyl vibration and further displaced by interaction with the 1373 cm.$^{-1}$ vibration of the acetoxy methyl group (cf. 1393 cm.$^{-1}$ band)
1300	—	—
1264	—	—
1238	Skeletal	See Reference 5
1115*	—	—
1097	—	—
1046	Skeletal	See Reference 5
1000	—	—
938	—	—
915	—	—
806	—	—
784	$-CH_2.CH_3$	—

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TABLE I (*Concluded*)

ν_{max}, cm.$^{-1}$	Group	Type of vibration
	B. $CD_3.CO.O.CD_2.CD_3$	
3460	$>C=O$	Overtone of carbonyl stretching vibration
2242	$-CD_2.CD_3$	Principally a $-CD_3$ vibration with some contribution from $-CD_2-$
2230	$-CD_2.CD_3$	Principally a $-CD_2-$ vibration with some contribution from $-CD_3$
2186	$-CD_2.CD_3$	Principally a $-CD_2-$ vibration but may be combined with an overtone of a skeletal band
2151	$-CD_2-$	—
2120	—	See text
2074	$-CD_3$ of ethoxy group	Symmetrical C—D stretching vibration (?)
1737	$>C=O$	Carbonyl stretching vibration
1194	$-CD_2.CD_3$	—
1178	$-CD_2.CD_3$	—
1097	$-CD_2.CD_3$	—
1082	$CD_3.CO-$	—
1059	$-CD_2.CD_3$	—
1047	$-CD_2.CD_3$	—
988	—	—
958	—	—
917	$CD_3.CO-$	—
815	—	—
780	—	—
718	—	—

**Inflection.*

(*a*) *The 2982 cm.$^{-1}$ band.*—This band occurs in light ethyl acetate with $\epsilon_{max}^{(a)}$74 and in $CD_3.CO.O.CH_2.CH_3$ with $\epsilon_{max}^{(a)}$71 (Figs. 1A, 1D). It also occurs in $CH_3.CO.O.CD_2.CH_3$ with $\epsilon_{max}^{(a)}$54 and in $CD_3.CO.O.CD_2.CH_3$ with $\epsilon_{max}^{(a)}$48 (Figs. 1B, 1F). It therefore appears that the CH_3 group of the ethoxy radical is mainly responsible for this absorption, but the intensity is enhanced in the $-CH_2.CH_3$ compounds. It will be shown later that this probably results from the superposition of an underlying $-CH_2-$ band.

(*b*) *The 2962 cm.$^{-1}$ inflection.*—This can be assigned to the methylene group, since it remains in $CH_3.CO.O.CH_2.CD_3$ and $CD_3.CO.O.CH_2.CD_3$ (Figs. 1C, 1G). In these spectra the 2962 cm.$^{-1}$ band exhibits asymmetry on the high frequency side, suggestive of an additional band. It is this component that enhances the intensity of the 2982 cm.$^{-1}$ band discussed in section (*a*) above.

(*c*) *The 2939 cm.$^{-1}$ band.*—This band is absent from $CH_3.CO.O.CH_2.CD_3$ and $CD_3.CO.O.CH_2.CD_3$ (Figs. 1C, 1G), and is therefore associated with the methyl group of the ethoxy radical. This is confirmed by comparison among Figs. 1B, 1D, 1E, and 1F.

(*d*) *The 2906 cm.$^{-1}$ band.*—This band is probably composite, with a weaker component on the low frequency side. In light ethyl acetate it occurs with $\epsilon_{max}^{(a)}$20 (Fig. 1A); it remains in $CH_3.CO.O.CH_2.CD_3$ and $CD_3.CO.O.CH_2.CD_3$ with $\epsilon_{max}^{(a)}$18 (Figs. 1C, 1G) and is therefore associated primarily with the methylene group. In $CH_3.CO.O.CD_2CH_3$ and $CD_3.CO.O.CD_2.CH_3$ (Figs. 1B,

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1F) the major component at 2906 cm.$^{-1}$ is removed and the weaker band appears at 2895 cm.$^{-1}$ with $\epsilon^{(a)}_{max}$ 9. This must be associated with the methyl group of the ethoxy radical.

(*e*) *The 2873 cm.*$^{-1}$ *band.*—This band must also be assigned to the methyl group of the ethoxy radical as it is missing from the spectra of $CH_3.CO.O.CH_2.CD_3$ and $CD_3.CO.O.CH_2.CD_3$ (Figs. 1C, 1G).

The more specific assignment of these bands to particular modes of vibration is difficult, although by analogy with the spectra of *n*-paraffin hydrocarbons (2) the primary component of the 2982 cm.$^{-1}$ band, and the 2873 cm.$^{-1}$ band, can probably be assigned respectively to the asymmetrical and symmetrical C—H stretching vibrations of the methyl group of the ethoxy radical. The 2906 cm.$^{-1}$ band shows analogy with the band at 2902 cm.$^{-1}$ in diethyl ketone (4) which has been assigned to the symmetrical C—H stretching vibration of the methylene group. This leaves the asymmetrical methylene C—H stretch for consideration, and this may account for the 2962 cm.$^{-1}$ inflection. The other absorption (notably the 2939 cm.$^{-1}$ band) would then be assigned to combination bands.

In these arguments it has been tacitly assumed that both the fundamental and the combination bands can be treated as localized in the individual methyl and methylene groups, and that they are not appreciably perturbed by deuteration at other centers in the molecule. This is substantiated by the summation spectra shown in Figs. 3A and 3B. By addition of the spectra of

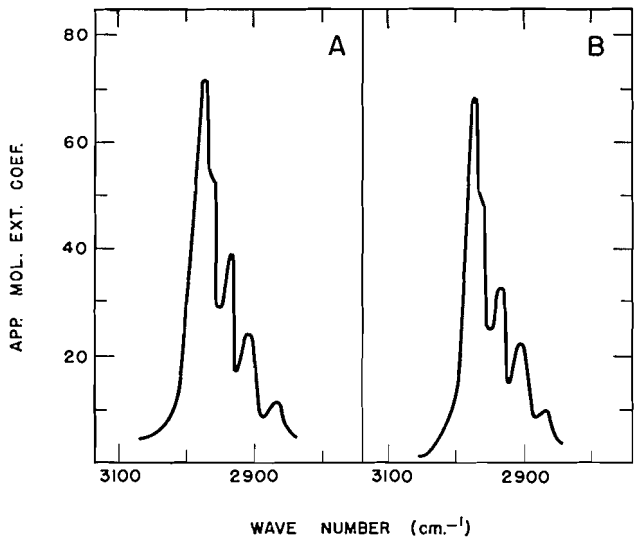

FIG. 3. Summation spectra.
A. $CH_3.CO.O.CD_2.CD_3 + CD_3.CO.O.CH_2.CD_3 + CH_3.CO.O.CD_2.CD_3$.
B. $CD_3.CO.O.CH_2.CD_3 + CD_3.CO.O.CD_2.CH_3$.

$CH_3.CO.O.CD_2.CD_3$, $CD_3.CO.O.CH_2.CD_3$, and $CD_3.CO.O.CD_2.CH_3$ the curve shown in Fig. 3A is obtained; this represents the composite absorption of the isolated methylene and two methyl groups, and it does in fact simulate the curve observed for light ethyl acetate (Fig. 1A), both qualitatively and

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quantitatively. The combination of the curves for $CD_3.CO.O.CH_2.CD_3$ and $CD_3.CO.O.CD_2.CH_3$ likewise simulates the spectrum of $CD_3.CO.O.CH_2.CH_3$ (cf. Figs. 3B and 1D).

Absorption Between 2850 and 2250 cm.$^{-1}$

In the spectra of the partly deuterated compounds a few weak bands ($\epsilon^{(a)}_{max} < 2$) are observed in this region as follows: $CH_3.CO.O.CD_2.CH_3$ (2510 cm.$^{-1}$); $CH_3.CO.O.CH_2.CD_3$ (2725, 2600, 2470 cm.$^{-1}$); $CD_3.CO.O.CH_2.CH_3$ (2620, 2470 cm.$^{-1}$); $CH_3.CO.O.CD_2.CD_3$ (2510 cm.$^{-1}$); $CD_3.CO.O.CD_2.CH_3$ (2545 cm.$^{-1}$); $CD_3.CO.O.CH_2.CD_3$ (2740, 2600, 2495 cm.$^{-1}$). These are probably overtones of skeletal vibrations, but it is curious that similar bands were not observed in the spectra of the light or the fully deuterated compound.

C—D Stretching Vibrations (2250–2050 cm.$^{-1}$)

Light ethyl acetate is transparent in this region (Fig. 4A) and does not exhibit any absorption near 2080 cm.$^{-1}$ comparable with the band in light methyl acetate which has been attributed to a skeletal overtone vibration (5). The fully deuterated ester (VIII) exhibits six bands at 2242, 2230, 2186, 2151, 2120, and 2074 cm.$^{-1}$ (Fig. 4H). As would be anticipated, this spectrum is

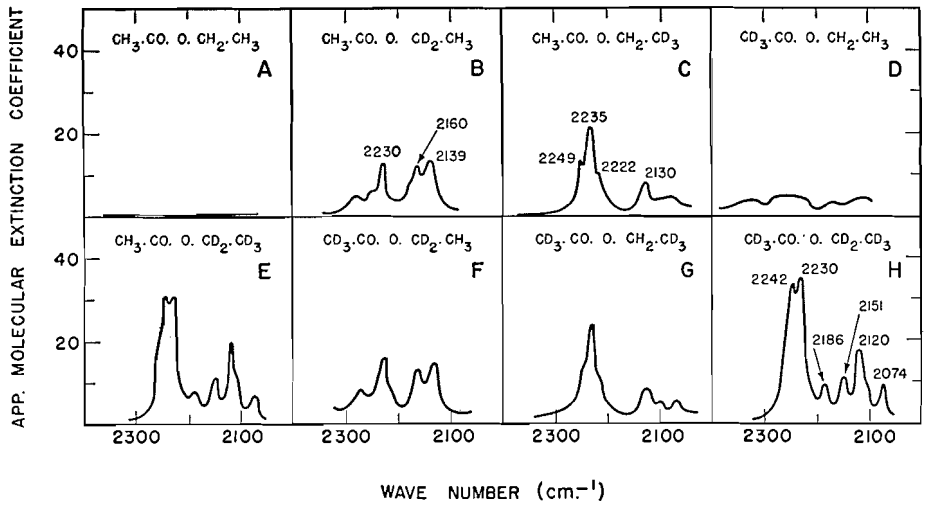

FIG. 4. Infrared spectra. Region of C—D stretching vibrations. (Carbon tetrachloride solution.)

almost identical with that of $CH_3.CO.O.CD_2.CD_3$ (Fig. 4E); the $CD_3.CO.O$— group therefore absorbs extremely weakly in this region. These bands are discussed individually below, and tentative assignments for the light compound and the fully deuterated compound are summarized in Table I. In general the assignments for the C—D stretching vibrations are less satisfactory than those for the C—H stretching vibrations and they seem less localized and more susceptible to perturbation effects of neighboring groups. This is indicated by the summation spectrum for $CD_3.CO.O.CH_2.CH_3$ + $CH_3.CO.O.CD_2.CH_3$ + $CH_3.CO.O.CH_2.CD_3$ which does not conform well with the spectrum observed for $CD_3.CO.O.CD_2.CD_3$ (Fig. 5).

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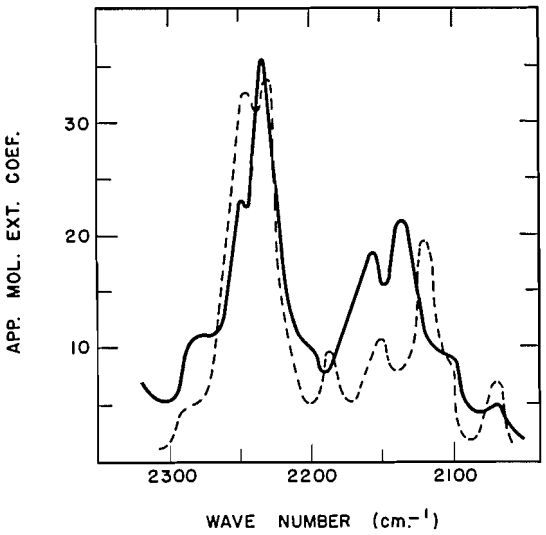

FIG. 5. ——— Summation spectrum of $CD_3.CO.O.CH_2.CH_3 + CH_3.CO.O.CD_2.CH_3 + CH_3.CO.O.CH_2.CD_3$.
– – – Observed spectrum of $CD_3.CO.O.CD_2.CD_3$.

(*a*) *The 2242–2230 cm.$^{-1}$ region.*—The absorption in this region is composite. The compounds containing $—O.CD_2.CD_3$ exhibit two peaks at 2242 and 2230 cm.$^{-1}$ both with extinction coefficients of about 30 units (Figs. 4E, 4H). In $CH_3.CO.O.CH_2.CD_3$ and $CD_3.CO.O.CH_2.CD_3$ (Figs. 4C, 4G), there is a weaker triplet at 2249, 2235, and 2222 cm.$^{-1}$, and in $CH_3.CO.O.CD_2.CH_3$ and $CD_3.CO.O.CD_2.CH_3$ (Figs. 4B, 4F) there is a single peak at 2230 cm.$^{-1}$ ($\epsilon^{(a)}_{max}$ 13–15). We may therefore regard the 2230 cm.$^{-1}$ band as coming principally from the dideuteromethylene group and the 2242 cm.$^{-1}$ band from the trideuteromethyl group, but there is appreciable overlap; possibly some mixing of the vibrations is also indicated by comparison with the summation spectrum in Fig. 5.

(*b*) *The 2186 cm.$^{-1}$ band.*—This appears only in molecules containing the $—CD_2.CD_3$ structure (Figs. 4E, 4H), but $CH_3.CO.O.CD_2.CH_3$ shows a weak inflection at 2177 cm.$^{-1}$ (Fig. 4B) which is also observable in the summation spectrum in Fig. 5 and this may contribute to the 2186 cm.$^{-1}$ band envelope.

(*c*) *The 2151 cm.$^{-1}$ band.*—This is probably a dideuteromethylene vibration; it is observed at this position only in $CH_3.CO.O.CD_2.CD_3$ and $CD_3.CO.O.CD_2.CD_3$ (Figs. 4E, 4H), but is probably similar to the bands at 2160 cm.$^{-1}$ in $CH_3.CO.O.CD_2.CH_3$ and at 2163 cm.$^{-1}$ in $CD_3.CO.O.CD_2.CH_3$ (Figs. 4B, 4F).

(*d*) *The 2140–2120 cm.$^{-1}$ absorption.*—All the deuterated ethyl acetates exhibit a band in this region; the position and intensity depends on the type of deuterium substitution in the ethoxy group, as shown in Table II. It does not seem possible to characterize these bands further at the present time.

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TABLE II

ABSORPTION AT 2140–2120 CM.$^{-1}$ IN DEUTERATED ETHYL ACETATES*

	ν_{max}, cm.$^{-1}$	$\epsilon^{(a)}_{max}$
$CH_3.CO.O.CD_2.CD_3$	2120	20
$CD_3.CO.O.CD_2.CD_3$	2120	18
$CH_3.CO.O.CD_2.CH_3$	2139	13
$CD_3.CO.O.CD_2.CH_3$	2134	13
$CH_3.CO.O.CH_2.CD_3$	2130	7
$CD_3.CO.O.CH_2.CD_3$	2130	8

Carbon tetrachloride solution.

(*e*) *The 2074 cm.$^{-1}$ band.*—This weak band is absent from the spectra of $CH_3.CO.O.CD_2.CH_3$ and $CD_3.CO.O.CD_2.CH_3$ (Figs. 4B, 4F) but present in all compounds containing a trideuteromethyl group in the ethoxy radical and it is obviously associated with the latter group (Figs. 4C, 4E, 4G, 4H).

C=O Stretching Vibrations (1742–1737 cm.$^{-1}$)

In light ethyl acetate the carbonyl stretching band occurs at 1742 cm.$^{-1}$ in carbon tetrachloride solution. The effect of increasing deuteration is shown in Table III. In general deuteration shifts the band to lower frequency, with the

TABLE III

DISPLACEMENT OF THE C=O STRETCHING AND THE PRINCIPAL SKELETAL FREQUENCY WITH DEUTERATION

	C=O stretching band,* cm.$^{-1}$	Skeletal band,† cm.$^{-1}$
$CH_3.CO.O.CH_2.CH_3$	1742	1235
$CH_3.CO.O.CH_2.CD_3$	1742	1238
$CH_3.CO.O.CD_2.CH_3$	1742	1263
$CD_3.CO.O.CH_2.CH_3$	1739	1254
$CH_3.CO.O.CD_2.CD_3$	1739	1264
$CD_3.CO.O.CH_2.CD_3$	1738	1251
$CD_3.CO.O.CD_2.CH_3$	1738	1277
$CD_3.CO.O.CD_2.CD_3$	1737	1275

*Carbon tetrachloride solution.
†Carbon disulphide solution.*

fully deuterated compound absorbing at 1737 cm.$^{-1}$. Deuteration in the acetoxy group appears to have a greater effect than deuteration in the ethoxy group.

All the compounds exhibit a weak band near 3460 cm.$^{-1}$ ($\epsilon^{(a)}_{max}$ 3–5) which is most probably the first overtone of this carbonyl band.

C—H Bending Vibrations (1500–1300 cm.$^{-1}$)

In this region light ethyl acetate exhibits six absorption bands (Fig. 6A); there is an additional inflection at 1430 cm.$^{-1}$ which only appears clearly when adjacent bands are eliminated by deuteration (Figs. 6C, 6E). These bands are

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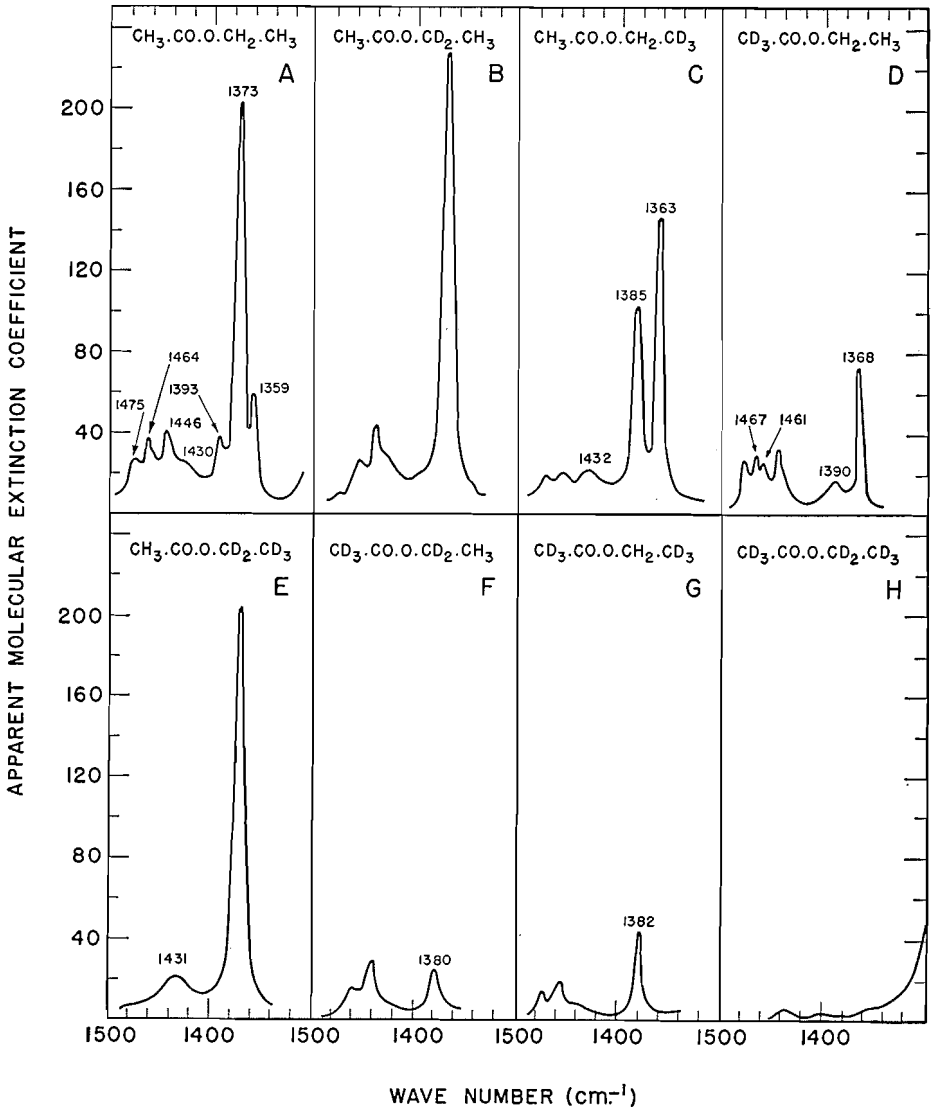

FIG. 6. Infrared spectra. Region of the most characteristic C—H deformation vibrations. (Carbon tetrachloride solution.)

all associated with C—H bending vibrations, as the spectrum of the fully deuterated compound shows no significant absorption in this region (Fig. 6H).

The assignments of these bands are summarized in Table I and they are considered individually below.

(*a*) *The 1475 cm.*$^{-1}$ *band.*—This is observed in the spectra of all molecules that contain the methylene group and it must therefore be assigned primarily to a —CH_2— vibration. However the band is appreciably stronger ($\epsilon_{max}^{(a)}$26) in compounds containing —$CH_2.CH_3$ (Figs. 6A, 6D) than in those containing

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—$CH_2.CD_3$ (Figs. 6C, 6G), for which $\epsilon^{(a)}_{max}$ is 14–18. There must therefore be a weak contribution from the ethoxy methyl group. This is substantiated by the spectrum of $CH_3.CO.O.CD_2.CH_3$ which exhibits a band with $\epsilon^{(a)}_{max}$ 10 at this position. No similar band, however, is observed in the spectrum of $CD_3.CO.O.CD_2.CH_3$.

(*b*) *The 1464 cm.$^{-1}$ band.*—In the light ester this band exhibits asymmetry on the low frequency side and it separates into a clear doublet at 1467 and 1461 cm.$^{-1}$ in $CD_3.CO.O.CH_2.CH_3$ (Fig. 6D). It is missing from the spectrum of $CH_3.CO.O.CD_2.CD_3$ (Fig. 6E) and would appear to involve superimposed absorption associated with the —CH_2— and —CH_3 groups of the ethoxy radical. In compounds containing —$CH_2.CD_3$ and —$CD_2.CH_3$ the band is displaced down to 1458 cm.$^{-1}$ (Figs. 6B, 6C, 6F, 6G).

(*c*) *The 1446 cm.$^{-1}$ band.*—This band is clearly associated with the methyl group of the ethoxy radical. It is present in the spectra of $CH_3.CO.O.CD_2.CH_3$, $CD_3.CO.O.CH_2.CH_3$, and $CD_3.CO.O.CD_2.CH_3$ (Figs. 6B, 6D, 6F), and absent from the spectra of $CH_3.CO.O.CH_2.CD_3$, $CH_3.CO.O.CD_2.CD_3$, and $CD_3.CO.O.CH_2.CD_3$ (Figs. 6C, 6E, 6G).

(*d*) *The 1430 cm.$^{-1}$ inflection.*—This band can be assigned to the methyl group of the acetoxy radical. It is present in the spectra of $CH_3.CO.O.CD_2.CH_3$, $CH_3.CO.O.CH_2.CD_3$, and $CH_3.CO.O.CD_2.CD_3$ (Figs. 6B, 6C, 6E), and absent from the spectra of $CD_3.CO.O.CH_2.CH_3$, $CD_3.CO.O.CD_2.CH_3$, and $CD_3.CO.O.CH_2.CD_3$ (Figs. 6D, 6F, 6G). It is clearly resolved in the spectra of the compounds that lack the overlapping 1446 cm.$^{-1}$ band (Figs. 6C, 6E).

The 1400–1350 cm.$^{-1}$ Absorption

The light compound exhibits three bands in this region; an intense band at 1373 cm.$^{-1}$ ($\epsilon^{(a)}_{max}$ 203) with weaker satellites at 1393 and 1359 cm.$^{-1}$.

The strong 1373 cm.$^{-1}$ band can be attributed to the $CH_3.CO$— group, as it is present with comparable intensity in $CH_3.CO.O.CD_2.CD_3$ (Fig. 6E), and with enhanced intensity ($\epsilon^{(a)}_{max}$ 222) in $CH_3.CO.O.CD_2.CH_3$ (Fig. 6B). The satellite bands must be associated with the ethoxy group, as they are absent from the spectrum of $CH_3.CO.O.CD_2.CD_3$ (Fig. 6E). However, the relationship is not a simple one, and a satisfactory rationalization is possible only if an appreciable wandering of these bands is recognized in the spectra of the various partly deuterated compounds.

In $CD_3.CO.O.CD_2.CH_3$ (Fig. 6F) there is a band at 1380 cm.$^{-1}$ assignable to the methyl group of the ethoxy radical and in $CD_3.CO.O.CH_2.CD_3$ (Fig. 6G) a somewhat stronger band at 1382 cm.$^{-1}$ which must be assigned to the methylene group. $CD_3.CO.O.CH_2.CH_3$ exhibits two bands at 1390 and 1368 cm.$^{-1}$ (Fig. 6D). These are suggestive of a Fermi resonance interaction between the 1380 and 1382 cm.$^{-1}$ bands observed for the "isolated" methyl and methylene groups with increase in frequency separation and redistribution of intensity. In the spectrum of $CH_3.CO.O.CD_2.CH_3$ (Fig. 6B) the intensity of the 1370 cm.$^{-1}$ band is increased, and it seems reasonable to presume that this results from the superposition of the 1373 cm.$^{-1}$ acetoxy methyl band on the ethoxy methyl band, with the latter displaced down by about 10 cm.$^{-1}$ from

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its position at 1380 cm.$^{-1}$ in $CD_3.CO.O.CD_2.CH_3$ (Fig. 6F). There still remains the spectrum of $CH_3.CO.O.CH_2.CD_3$ to be explained. Here there are two bands of medium intensity at 1385 and 1363 cm.$^{-1}$ (Fig. 6C) and to account for these we must presume interaction between the 1382 cm.$^{-1}$ methylene band and the 1370 cm.$^{-1}$ acetoxy methyl band, in the course of which the separation increases and the higher frequency band (predominantly methylene) gains intensity at the expense of the lower frequency (predominantly methyl) band.

These spectra are considerably more complex than those of methyl acetate discussed previously (5). This is probably because the symmetrical C—H bending vibration of the —$O.CH_3$ group in methyl acetate is displaced up to 1435 cm.$^{-1}$ where it does not perturb the corresponding vibration of the acetoxy methyl group at 1369 cm.$^{-1}$.

The more detailed assignment of these ethyl acetate bands to specific modes of vibration within the alkyl groups is difficult, and must be treated very circumspectly. From analogy with the *n*-paraffin hydrocarbons we would expect to find two C—H bending vibrations associated with each methyl group, and one (scissoring) C—H bending vibration of the methylene group. The situation is comparatively clear with respect to the acetoxy methyl group for which we can assign the asymmetrical C—H bending vibration to the 1430 cm.$^{-1}$ band and the symmetrical vibration to the 1373 cm.$^{-1}$ band. The methylene scissoring vibration probably provides the —CH_2— component of the 1463 cm.$^{-1}$ band. The 1446 cm.$^{-1}$ band would likely be the asymmetrical C—H bending vibration in the ethoxy methyl group while the corresponding symmetrical vibration mixes with a methylene C—H vibration to give the 1393, 1359 cm.$^{-1}$ doublet. This methylene vibration could be the wagging mode displaced up from its position near 1307 cm.$^{-1}$ in *n*-paraffin hydrocarbons by a vicinal effect of the oxygen atom. The remaining bands must perforce be assigned to combination bands.

Absorption Below 1300 cm.$^{-1}$

The spectra in the range 1300–700 cm.$^{-1}$ are shown in Figs. 7A–7H for solutions in carbon disulphide. As with the methyl acetates, it is possible to recognize systematic changes in these spectra on selective deuteration. Most prominent is the strong skeletal band that occurs at 1238 cm.$^{-1}$ in the spectrum of the light compound. As in methyl acetate, this shifts upwards on deuteration, but the displacements do not in all cases correlate with the decrease in the C=O stretching frequency (Table III) the principal exceptions being $CH_3.CO.O.CD_2.CH_3$ and $CD_3.CO.O.CH_2.CD_3$.

The second strongest band, at 1046 cm.$^{-1}$, in light ethyl acetate (Fig. 7A) obviously parallels the band at 1047 cm.$^{-1}$ in light methyl acetate, but is more sensitive to perturbation on deuteration. It is clearly present at 1034 cm.$^{-1}$ in the spectrum of $CH_3.CO.O.CH_2.CD_3$ (Fig. 7C), but is not obviously recognizable in the other deuterated analogues. It might be tentatively identified with the band at 1124 cm.$^{-1}$ in $CH_3.CO.O.CD_2.CH_3$ and $CD_3.CO.O.CD_2.CH_3$ (Figs. 7B, 7F), which is accompanied by weaker bands at 1164 and 1144 cm.$^{-1}$, forming a triplet characteristic of the —$O.CD_2.CH_3$ system.

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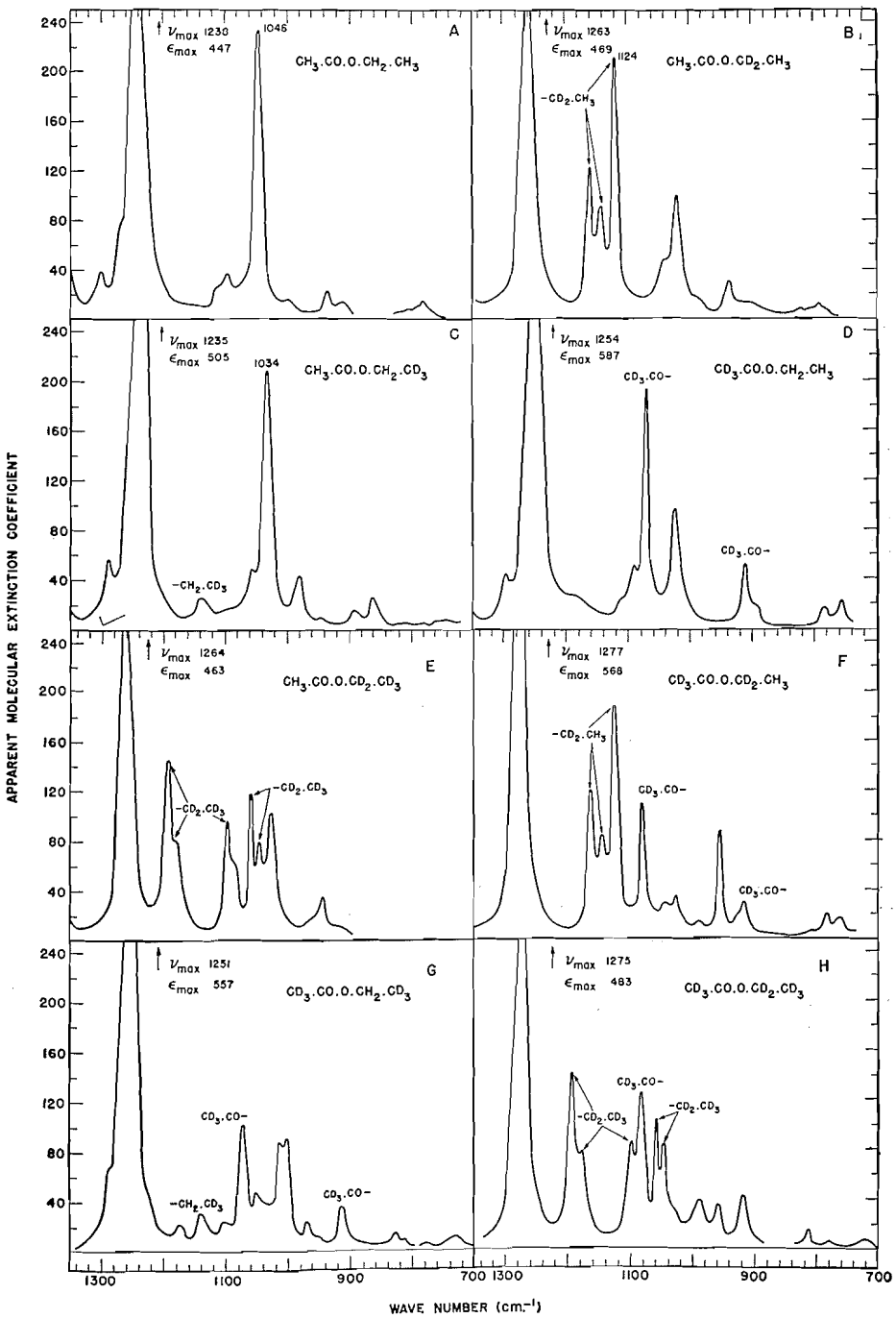

FIG. 7. Infrared spectra. "Fingerprint region". (Carbon disulphide solution.)

A comparison among the spectra reveals several other bands characteristic of the various deuterated and partly deuterated alkyl groups. These are summarized in Table I and indicated on the curves in Figs. 7B–7G. In most cases these bands are too intense to be attributed to pure C—D deformation vibrations displaced down from the 1500–1300 cm.$^{-1}$ region; the majority of them also occur between 1200 and 1000 cm.$^{-1}$ whereas the simple $\sqrt{2}$ displacement factor would place such bands in the 1050–900 cm.$^{-1}$ range. It is probable that they arise mainly from the interaction of C—D deformation modes with skeletal vibrations. This adds support to the generalization that in such deuteration studies it is relatively easy to observe the disappearance of bands associated with C—H vibrations, but only rarely can the corresponding C—D vibration be identified with certainty.

CONCLUDING REMARKS

In the course of a study of the intensities of some characteristic bands in ketones and esters, Francis (1) assigned a few of the bands in light ethyl acetate. These assignments, which were limited to the 2982, 2939, 1393, 1373, and 1359 cm.$^{-1}$ bands, agree with ours, although Francis from the spectrum of the light acetate alone was not in a position to recognize the perturbations associated with the 1393–1359 cm.$^{-1}$ absorption. To our knowledge the partly deuterated ethyl acetates have not been prepared previously and the spectra are recorded here for the first time.

ACKNOWLEDGMENTS

We are very grateful to Mr. Armand Nadeau for technical assistance with the measurement of the spectra.

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THE SYSTEM $LiNO_3$–C_2H_5OH–H_2O AT 25°C.[1]

By A. N. Campbell and E. M. Kartzmark

ABSTRACT

Lithium nitrate does not form solid alcoholates at 25°C. The hydrate consisting of one molecule of nitrate to half a molecule of water, which is claimed to exist by Donnan and Burt, appears not to exist. Not only does this half hydrate not appear on the 25° isotherm but it cannot be detected dilatometrically at any temperature.

The work of Campbell and Debus on the conductances of lithium nitrate solutions in alcohol–water mixtures (1) has led us to suppose that at a concentration of alcohol lying between 30 and 70% by weight of alcohol, the solvation of the lithium ion changes from a water solvation to an alcohol solvation. Since lithium nitrate forms a hydrate, $LiNO_3.3H_2O$, it seemed an obvious course to investigate whether this salt also forms one or more solid alcoholates, by investigating the equilibrium diagram of the system $LiNO_3$–C_2H_5OH–H_2O at 25°C.

No solid alcoholate was found. It does not by any means follow that the lithium ion is not alcoholated. It is sufficient to say that, if a solid compound of lithium nitrate and alcohol does exist, its melting point is below 25°C., and, if the chemical nature of the alcohol molecule is compared with that of the water molecule, this is inherently probable.

We were surprised to find that, though trihydrate and anhydrous lithium nitrate appeared as solid phases on our diagram, there was never any indication of the half hydrate, claimed by Donnan and Burt (2), as a solid phase. After many attempts to obtain this hydrate and use it as an inoculant, we finally concluded that it does not exist. Donnan and Burt base their claim for the existence of this hydrate on the doubtful procedure of crystallizing at 40° (above the transition temperature of the trihydrate), filtering, and analyzing the solid. Their solubility curve shows a slight break at their assumed transition temperature of 61°C. In addition they claim a change in dilatometer expansion about this temperature.

EXPERIMENTAL

Schreinemakers' "wet rest" method was used for the investigation of the solubility isotherm. Alcohol was determined by distillation, dilution of distillate to a fixed volume of 100 ml., and determination of the density. Reference to standard tables for the density of ethyl alcohol – water mixtures then gave the alcohol content. Lithium nitrate was determined by evaporation of the residue from the distillation to dryness, followed by melting of the solid to drive off the last traces of water.

In order to investigate the claim of Donnan and Burt that the change from the half hydrate to the anhydrous form, at 61°C., can be detected dilato-

[1]*Manuscript received June 22, 1956.*
Contribution from the Department of Chemistry, University of Manitoba, Winnipeg, Manitoba.

metrically, we made up a mixture of the stoichiometric composition of the half hydrate and placed some 50 gm. of this mixture in the bulb of a dilatometer, using *m*-xylene as indicator fluid; the temperature was then raised slowly and the height of the xylene column followed with a cathetometer. The change of the trihydrate (to half hydrate or anhydrous salt) is readily observed about 30°C., since it is accompanied by a large increase in volume. On further heating to 75°, however, no trace of discontinuity could be detected on the height vs. temperature curve. Our dilatometer was a very delicate one and it is impossible that any expansion or contraction, however slight, could have escaped us. It is possible that the half hydrate continued to exist metastably above its transition temperature but this is most unlikely.

RESULTS

Our solubility results are contained in Table I.

TABLE I

COMPOSITIONS OF SATURATED SOLUTIONS AND "WET RESTS" AT 25.0°C.

Solution, % by wt.		"Wet rest", % by wt.		Nature of solid phase
C_2H_5OH	$LiNO_3$	C_2H_5OH	$LiNO_3$	
—	47.8	—	55.4	$LiNO_3.3H_2O$
0.9	47.3	Trace	55.3	"
5.0	47.0	0.7	56.4	"
11.6	47.8	1.4	56.5	"
13.5	49.2	2.8	55.2	"
14.1	51.9	6.8	54.0	"
11.2	53.5	2.5	55.7	"
6.9	58.0	2.7	66.9	$LiNO_3.3H_2O + LiNO_3$
6.6	58.4	1.8	90.2	$LiNO_3$
10.3	55.7	Trace	97.7	"
16.9	53.2	4.0	90.4	"
35.8	44.5	9.0	85.6	"
60.0	32.8	12.2	86.2	"
72.9	26.3	10.7	89.2	"

NOTE: *The results are expressed graphically in Fig. 1.*

DISCUSSION

It is apparent from Fig. 1 that no alcoholate appears as solid phase at 25.0°.

The isotherm gives no indication of the hydrate, $LiNO_3.\frac{1}{2}H_2O$, claimed to exist by Donnan and Burt (2). The dilatometric experiments also show no indication of a phase change in the region claimed by Donnan and Burt for the change: $LiNO_3.\frac{1}{2}H_2O = LiNO_3 + \frac{1}{2}H_2O$. It is also significant, in our opinion, that the composition of the peritectic point, on the equilibrium diagram of Donnan and Burt, is very far removed from the composition of the half hydrate.

The form of the solubility curve of the trihydrate on the 25° isotherm is what would be expected, bearing in mind that the trihydrate melts congruently at about 29°C. The form of this re-entrant curve means, as the figures of

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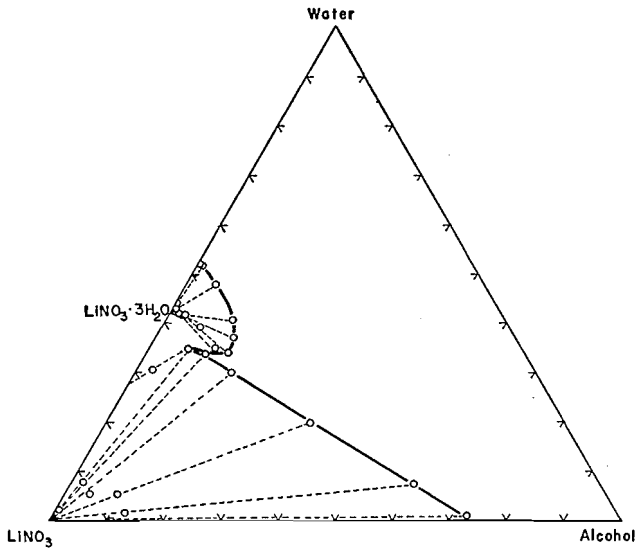

FIG. 1. The system $LiNO_3$–C_2H_5OH–H_2O; 25° isotherm.

Table I show, that the solubility of lithium nitrate in water is increased to a maximum by the addition of alcohol (from 47.8% in pure water to 58.0% for 6.9% alcohol).

The single isothermal invariant point occurring on the diagram, corresponding to the coexistence of lithium nitrate trihydrate and anhydrous lithium nitrate, has a concentration of 6.9% alcohol and 58.0% lithium nitrate.

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DIPHENYLCYANAMIDE DERIVATIVES

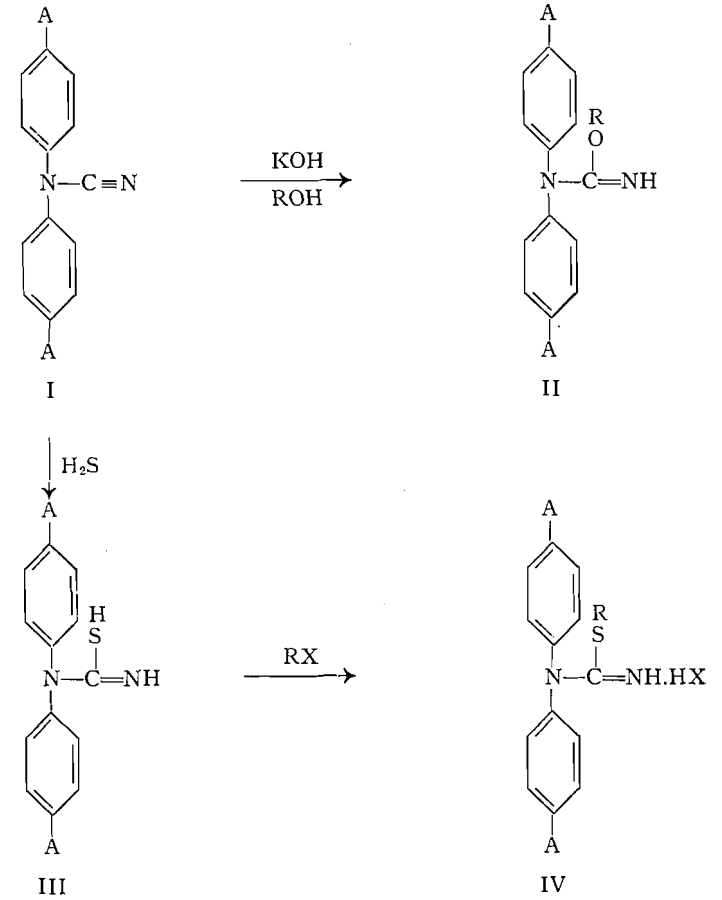
III. 2-THIOPSEUDOUREAS[1,2]

By Ronald E. Beals[3] and William H. Brown[4]

ABSTRACT

Diphenylalkylthiopseudourea hydrohalides and dichlorodiphenylalkylthiopseudourea hydrohalides are formed when the corresponding thiourea is treated with an alkyl halide. The thiourea is prepared by the addition of hydrogen sulphide to the corresponding cyanamide compound. The hydrohalides are unstable in the presence of alkali.

INTRODUCTION



[1]*Manuscript received May 29, 1956.*
Contribution from the Department of Chemistry, Ontario Agricultural College, Guelph, Ontario.
[2]*The terms "isourea" and "isothiourea" are no longer used by Chemical Abstracts. The names "pseudoureas" and "2-thiopseudoureas" are used. The compounds are numbered according to the scheme:* $\overset{1}{HN}=\overset{2}{C}(OR)-\overset{3}{NH_2}$.

[3]*Holder of a C.I.L. Fellowship 1954–55. Present address: Canadian Industries (1954) Limited, Toronto, Ontario.*
[4]*Associate Professor of Chemistry, Ontario Agricultural College, Guelph, Ontario.*

When diphenylcyanamide (I: A = H) is hydrolyzed in the presence of hydroxylated solvents, of the type ROH, stable pseudoureas (II: A = H) are formed (10). Similarly, di-*p*-chlorophenylcyanamide (I: A = Cl) yields the chlorinated pseudourea (II: A = Cl). These latter compounds (II: A = Cl, R = Me or Et) have been shown to be physiologically active (2).

Since thioureas and thiopseudoureas have shown promise as organic fungicides (1, 3, 6), it was of interest to prepare the sulphur analogues of II.

DISCUSSION

Various methods for the preparation of 3,3-diphenyl-2-thiourea (III: A = H) have been previously employed (4, 9, 11). In particular, Kurzer (8) has prepared the compound by the addition of hydrogen sulphide to diphenylcyanamide in ethanol solution in the presence of ammonia.

In the present investigation it has been found that hydrogen sulphide adds to diphenylcyanamide (I: A = H) in the presence of dimethylamine and sodium ethoxide to form 3,3-diphenyl-2-thiourea (III: A = H). Also, 3,3-di-*p*-chlorophenyl-2-thiourea (III: A = Cl) is formed when di-*p*-chlorophenylcyanamide (I: A = Cl), prepared by the method of Robinson and Brown (10), is treated with hydrogen sulphide under the same conditions.

When 3,3-diphenyl-2-thiourea (III: A = H) is treated with ethyl iodide, the product is 3,3-diphenyl-2-ethyl-2-thiopseudourea hydroiodide (IV: A = H, R = Et, X = I). In the same manner 3,3-diphenyl-2-ethyl-2-thiopseudourea hydrobromide (IV: A = H, R = Et, X = Br) and 3,3-diphenyl-2-methyl-2-thiopseudourea hydroiodide (IV: A = H, R = Me, X = I) were produced from the corresponding alkyl halides. No product is obtained if the alkyl halide used is a chloride or a branched chain alkyl bromide.

Similarly, when 3,3-di-*p*-chlorophenyl-2-thiourea (III: A = Cl) is treated with an alkyl halide the product is the corresponding 2-alkyl-2-thiopseudourea hydrohalide (IV: A = Cl).

In all cases, alkaline decomposition of IV yields the corresponding alkanethiol and the corresponding diphenylcyanamide.

Treatment of either the 3,3-diphenyl-2-alkyl-2-thiopseudourea hydrohalide (IV: A = H) or the 3,3-di-*p*-chlorophenyl-2-alkyl-2-thiopseudourea hydrohalide (IV: A = Cl) in ethanol with aqueous picric acid solution results in the formation of the corresponding stable picrate.

In Table I are listed the 2-thiopseudourea hydrohalides and picrates prepared as well as their properties.

For fungicidal evaluation tests refer to the work of Kempton (5).

EXPERIMENTAL

All melting points have been corrected against reliable standards. Molecular weights were determined by the Rast method. A typical preparative method is given for a 2-thiopseudourea hydrohalide. All the others listed in Table I may be obtained by a similar procedure.

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TABLE I

2-THIOPSEUDOUREA HYDROHALIDES AND PICRATES

Compound IV	M.P.	Yield, %	Stability (stable below)	Mol. formula	Analysis	
					Calculated	Found
A = H, R = Me, X = I	159.5–160.0°	67	5°	$C_{14}H_{15}IN_2S$	I, 34.2; mol. wt., 369	I, 34.2; mol. wt., 368
A = H, R = Et, X = I	85.0–86.0°	99	5°	$C_{15}H_{17}IN_2S$	I, 32.8; mol. wt., 384	I, 32.1; mol. wt., 394
A = H, R = Et, X = Br	169.5–170.0°	81	25°	$C_{15}H_{17}BrN_2S$	Br, 23.6; mol. wt., 337	Br, 22.7; mol. wt., 350
A = H, R = Me, X = Pic.	166.0–166.5°	72	25°	$C_{20}H_{17}N_5O_7S$	N,14.9	N, 14.1
A = Cl, R = Me, X = I	200°	90	25°			
A = Cl, R = Et, X = I	133.0–134.5°	90	5°			

3,3-Diphenyl-2-thiourea (III: A = H)

A solution of 0.90 gm. (0.020 mole) of anhydrous dimethylamine (E.K. 601) and 0.46 gm. (0.020 mole) of sodium in 100 ml. of absolute ethanol was cooled to −8° C. and saturated with hydrogen sulphide gas at this temperature. The solution was treated with 5.0 gm. (0.026 mole) of diphenylcyanamide, prepared according to the procedure of Kurzer (7). Hydrogen sulphide was again passed into the mixture for 10 min. The mixture was placed in a Pyrex bottle as found in a Parr low-pressure hydrogenation apparatus and securely stoppered. The mixture was heated to 80–90° C. with occasional shaking. The pressure varied between 60–80 p.s.i.g. After four hours, the ethanol was removed by evaporation. The solid brown residue was crystallized from ethanol yielding 3.0 gm. (35%) of white needles, m.p. 218° C. The compound is insoluble in water, sodium hydroxide, and hydrochloric acid and soluble in acetone, ethanol, and chloroform. A mixture melting point with a sample of 3,3-diphenyl-2-thiourea, prepared by the method of Passing (9), showed no depression.

3,3-Di-p-chlorophenyl-2-thiourea (III: A = Cl)

A solution of 0.10 gm. (0.004 mole) of sodium and 0.50 gm. (0.011 mole) of anhydrous dimethylamine in 25 ml. of absolute ethanol in a "Coca-Cola" bottle was cooled to −5.0° C. and saturated with hydrogen sulphide gas. To this solution was added 1.0 gm. (0.0038 mole) of di-*p*-chlorophenylcyanamide prepared according to the procedure of Robinson and Brown (10). The bottle was then capped and placed in a water bath at 80–86° C. for four hours. After cooling there remained in the bottle a heavy yellow precipitate. The mixture was filtered and the residue washed with cold ethanol. Crystallization from ethanol gave 0.99 gm. (86%) of fine white needles, m.p. 195.5° C. Qualitative analysis gave positive tests for nitrogen, halogen, and sulphur. The compound is insoluble in water, sodium hydroxide, and hydrochloric acid. It is soluble in ethanol, ether, and chloroform. Anal. Calc. for $C_{13}H_{10}Cl_2N_2S$: Cl, 23.9; N, 9.44; mol. wt., 297. Found: Cl, 23.9; N, 9.46; mol. wt., 294.

3,3-Diphenyl-2-methyl-2-thiopseudourea Hydroiodide (IV: A = H, R = Me, X = I)

A solution of 0.50 gm. (0.002 mole) of 3,3-diphenyl-2-thiourea in 30 ml. of benzene was treated with 2.3 gm. (0.016 mole) of methyl iodide. The solution was refluxed for 23 hr. and when cooled, a precipitate formed which weighed 0.55 gm. (67%). The solid, after being washed with benzene, melted at 159.5–160.0° C. Qualitative analysis showed the presence of halogen, sulphur, and nitrogen. The compound is soluble in water, hydrochloric acid, and ethanol. It decomposes in ether and sodium hydroxide and is unstable unless stored at temperatures below 5° C. Anal. Calc. for $C_{14}H_{15}IN_2S$: I, 34.2; mol. wt., 369. Found: I, 34.2; mol. wt., 368.

Alkaline Decomposition of 3,3-Diphenyl-2-methyl-2-thiopseudourea Hydroiodide (IV: A = H, R = Me, X = I) *to Yield Methanethiol and Diphenylcyanamide*

A solution of 0.20 gm. of IV: A = H, R = Me, X = I in 10 ml. of ethanol was treated with 10 ml. of a 5% aqueous sodium hydroxide solution. A precipi-

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tate formed immediately. It weighed 0.10 gm. and was shown to be diphenylcyanamide by mixture melting point. To the filtrate was added 1.0 gm. of 2,4-dinitrochlorobenzene in ethanol and the mixture was refluxed for five minutes. On cooling a fluffy yellow precipitate formed. The precipitate, after being crystallized twice from ethanol, melted at 128° C. A mixture melting point with authentic 2,4-dinitrophenyl-methyl-sulphide showed no depression.

ACKNOWLEDGMENTS

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PERIODATE–PERMANGANATE OXIDATIONS

V. OXIDATION OF LIPIDS IN MEDIA CONTAINING ORGANIC SOLVENTS[1]

By E. von Rudloff

ABSTRACT

The periodate–permanganate reaction with methyl oleate and triolein has been studied in media containing a variety of organic solvents. The oxidation proceeded favorably in media containing tertiary butanol or pyridine and conditions have been found which permit the quantitative analysis of unsaturated lipids.

INTRODUCTION

The quantitative oxidation of unsaturated fatty acids to specific and easily identifiable end products was described previously (8). It was shown that the periodate–permanganate oxidation of such acids adheres strictly to the reaction scheme

$$R.CH{=}CH.(CH_2)_n.CO_2H + 4[O] \rightarrow R.CO_2H + HO_2C.(CH_2)_n.CO_2H.$$

Erucic acid, methyl esters, and triglycerides were not soluble in the weakly alkaline, dilute aqueous reaction mixture (5) and did not give satisfactory results. The solubility of these lipids was increased by using a modified reagent (7) containing pyridine, and quantitative results could be obtained in the oxidation of erucic acid and methyl linoleate. Methyl oleate and triolein, however, were incompletely oxidized under these conditions (8).

Conditions have now been found which permit the quantitative oxidation of these latter unreactive compounds. Thus when methyl oleate was shaken in media containing 20 to 50% pyridine and a small amount of potassium carbonate, oxidant equivalent to the theoretical value of four oxygen atoms was consumed in three to six hours' reaction time (Table I), and this value was not appreciably exceeded during three days' reaction time. Chromatographic analysis of the saponified oxidation products gave pelargonic and azelaic acids in 96 and 98% (±1%) of the theoretical yield respectively. The quantitative oxidation of triolein in media containing pyridine was not possible, mainly because of the very low rate of reaction (Table I). Increasing the rate of oxidation by employing higher temperatures, pH, or concentrations of permanganate (5) was not feasible because of overoxidation after correspondingly shorter reaction times. Virtually theoretical results, however, were obtained with triolein, as well as with methyl oleate, by using tertiary butanol – water as solvent (Table I), and 98 to 99% of the calculated amount of azelaic acid was isolated after four to eight hours' reaction time.

Oleodistearin reacted to completion in media containing 60% tertiary butanol (Table I), and sunflower-seed oil and linseed oil, i.e. triglycerides

[1]*Manuscript received in original form March 7, 1956, and as revised, June 22, 1956.*
Contribution from the National Research Council of Canada, Prairie Regional Laboratory, Saskatoon, Saskatchewan. Issued as Paper No. 228 on the Uses of Plant Products and as N.R.C. No. 4055.

TABLE I

RATE OF REACTION OF LIPIDS (EXPRESSED AS AMOUNT OF OXIDANT CONSUMED IN PER CENT OF THE CALCULATED THEORETICAL AMOUNT) IN MEDIA CONTAINING PYRIDINE OR TERTIARY BUTANOL

	Reaction time, hr.						pH
	½	1	3	6	24	48	at start*
Methyl oleate in:							
10% pyridine soln.	—	4	10	18	58	—	7.5
20% " "	—	38	80	96	100	102	8.0
30% " "	—	68	90	100	101	100	8.2
40% " "	—	83	99	100	100	100	8.3
50% " "	—	80	96	100	99	102	8.3
20% *tert*-butanol soln.	5	10	26	—	—	—	7.2
30% " " "	85	100	100	—	103	—	7.6
40% " " "	90	100	100	—	107	—	8.1
60% " " "	40	68	93	—	107	—	8.4
Triolein in:							
40% pyridine soln.	—	—	4	8	25	—	8.5
40% *tert*-butanol soln.	—	12	22	27	48	63	8.1
50% " " "	10	21	73	98	98	104	8.2
60% " " "	16	37	86	100	102	106	8.4
70% " " "	12	27	65	83	98	104	8.4
Oleodistearin in:							
60% *tert*-butanol soln.	—	40	75	83	95	96	8.3

**At the end of the reaction the pH had dropped by 0.3 to 0.5 units.*

containing polyunsaturated acids, reacted at about the same rate in media containing either tertiary butanol or pyridine. It, therefore, appears possible to oxidize quantitatively both reactive and unreactive unsaturated lipids, including fatty acids, their methyl esters and triglycerides, by using either an aqueous solution of the periodate–permanganate reagent, or solutions containing various amounts of tertiary butanol or pyridine. These methods may also provide an accurate and convenient means for determining the amount of saturated lipids in mixtures containing unsaturated ones.

Acetone (1) and pyridine (2, 3, 6, 9) have frequently been employed as solvents in permanganate oxidations, and glycol cleavage has been effected by periodate in a variety of solvents, including alcohols, esters, and acids (4). These and other solvents were examined for suitability with the combined periodate–permanganate reagent, and tertiary butanol and pyridine were found to be most satisfactory for the oxidation of lipids. Tertiary butanol gave results which were in many respects superior to those obtained with the latter solvent, but overoxidation occurred after shorter reaction times (Table I). The oxidation of methyl oleate proceeded less favorably in media containing dimethyl formamide, butyro lactone, or acetone and was very much slower when methyl acetate, ethyl acetate, 2-methoxy ethanol acetate, and dioxane were used. The oxidation was rapid in media containing alcohols, but methanol,

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ethanol, isopropanol, and 2-methoxy ethanol were themselves oxidized at a comparatively high rate. Tetrahydrofuran and formamide were degraded extensively by the reagent.

Pyridine and tertiary butanol consumed oxidant at a low rate even after repeated purification, and this blank consumption decreased with a decrease in initial concentration of oxidant. Hence, a correction was necessary to account for the higher concentration of oxidant in blank determinations than was present in corresponding solutions containing the compound to be oxidized, once the latter had consumed oxidant. This correction was negligibly small in reaction times of less than six hours, but became increasingly more important after longer periods of reaction. Because an exact correction was not possible, the margin of error increased from about 1% to 3% and more. The amount of oxidant consumed in blank determinations increased slightly with increasing concentrations of tertiary butanol, but was practically constant with 10 to 50% pyridine.

To prevent a drop of the pH to below 6 by the formation of acidic end products, sufficient potassium carbonate was added to neutralize these acids (5, 8). When potassium carbonate was present in blank determinations with tertiary butanol the amount of oxidant consumed increased slightly. A very marked increase, however, was found when pyridine was used, e.g. using 10% pyridine and potassium carbonate (15 mgm. per aliquot of 10 ml.) the reaction mixture decolorized after six hours' reaction time with the consumption of more than 10% of oxidant. With increasing concentrations of pyridine this effect decreased noticeably and was no longer apparent when 40% pyridine was present. Also, although an initial increase in the concentration of potassium carbonate resulted in an increase in the rate of oxidation of pyridine, no further change was observed when more than 15 mgm. per aliquot (up to 30 mgm.) was added. The increase of the rate of oxidation cannot be explained solely as a pH effect (5), and appears to be due to catalysis, and may merit further study.

In the presence of potassium carbonate the oxidant precipitated partially when 50% or more tertiary butanol or pyridine was used and this precipitate did not react readily with arsenite solution in the cold. Heating on a steam bath for about one hour gave complete reduction, and thus reproducible results, when tertiary butanol was present, and this solvent could be employed advantageously in concentrations up to 70%. When more than 50% pyridine was used the results were not consistent. The degree of oxidation of methyl oleate and triolein in such media was, therefore, determined by the amount of azelaic acid obtained. The results showed that the rate of oxidation decreased when more than 50% pyridine was present and it was concluded that the most favorable range of pyridine concentration for the oxidation of lipids was from 30 to 50%.

The reaction mixtures described above are probably heterogeneous at the outset and the manner of addition of the compound to be oxidized is important, since rapid addition, or addition before enough solvent was present, frequently

resulted in the lipid separating in droplets. Also, in some experiments on a larger scale the rate of oxidation was lower.

Although the object of the present study was to find reaction conditions for the quantitative oxidation of unsaturated lipids, it is conceivable that the modifications of the periodate–permanganate reagent described herein may find application to other classes of compounds which are insoluble in the aqueous reagent. The fact that terpenes reacted equally well in media containing pyridine or dioxane (7) indicates that the choice of solvent need not necessarily be limited to tertiary butanol and pyridine.

EXPERIMENTAL

Analytical grade reagents were used and all solvents were fractionally distilled in a Podbielniak column. Pyridine and dioxane were purified by conventional methods. Further purification was achieved by reacting under nitrogen with 2 to 10 ml. concentrated periodate–permanganate reagent per liter of solvent. After the mixture was left at room temperature for at least six hours the excess oxidant was reduced and the solvent was distilled under nitrogen and over solid potassium hydroxide. Pyridine thus purified did not deteriorate noticeably within two weeks when stored in a brown, glass stoppered flask, and in blank determinations less oxidant was consumed than was previously reported (7).

The stock oxidant solution consisted of 20.86 gm. (97.5 mM.) sodium metaperiodate and 250 ml. 0.01 *M* (2.5 mM.) potassium permanganate per liter. The test compounds had the following iodine values:

Methyl oleate—found: 85.6; calculated: 85.61.
Triolein —found: 85.2; calculated: 85.90.
Oleodistearin —found: 26.7; calculated: 28.54; m.p. 35°–36° C.

Melting points were obtained on a hot-stage microscope and are corrected.

Standard Procedure of Oxidation

Stock oxidant solution, 2.0 ml., was placed in a 125 ml. stoppered flask and to this was added 1.0 ml. aqueous solution containing 2.5 mgm. potassium carbonate, water, and solvent to give 9.0 ml. of a solution which contained 1.0 ml. less solvent than was desired in the final reaction mixture. To this was added slowly with shaking 1.0 ml. of a solution of methyl oleate, 1.25 mM. per 100 ml. solution in the corresponding solvent, and the time of addition was noted. When triolein was oxidized 1.0 ml. of a solution containing 0.4167 mM. per 100 ml. solution was employed, and with sunflower-seed oil and linseed oil correspondingly smaller amounts were used to keep the concentration of oxidant about twice that required theoretically. The flask was stoppered and put onto a shaker for the required reaction time. A corresponding blank experiment was started at the same time. The temperature of reaction was 24° C. (±2°).

After the desired time of reaction, the oxidation was stopped by addition, with shaking, of sodium bicarbonate, 0.5 to 1 gm., followed immediately by

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5.0 ml. 0.1 *N* sodium arsenite solution. A few crystals of potassium iodide were added after all permanganate color had disappeared, and the aliquots were allowed to stand at least 15 min. When 40% or less solvent was present, the aliquots were diluted with 30 to 40 ml. water, and were then titrated slowly to the starch end point with 0.015 *N* iodine solution. Duplicate determinations agreed within 0.10 ml. iodine solution when pyridine was used, and 0.20 ml. when tertiary butanol was present. The solutions containing tertiary butanol were easily overtitrated, and it was found advantageous to evaporate most of the solvent before titration. At higher concentrations of solvent the flasks containing the reduced reaction mixtures were placed on a steam bath for one-half to one hour, cooled to room temperature, and diluted and titrated as before. Duplicate determinations agreed within 0.20 to 0.30 ml. iodine solution, but when more than 50% pyridine was used, the error became larger.

Oxidation and Isolation of End Products

The same oxidation procedure as above was used, taking 10 to 20 times the amount of reactants and solvents. The reaction was stopped one to two hours after the required minimum for complete reaction by the addition of enough sodium metabisulphite to reduce all iodine to iodide. Potassium hydroxide, 1 to 2 gm., was added and the flask was put on a rotary evaporator, the temperature being kept at about 50° C. During the course of the one and one-half to two hours the organic solvent was completely evaporated whilst any ester was saponified simultaneously. The solution was acidified strongly with 10% sulphuric acid and then extracted continuously with ethyl ether for 8 to 10 hr. The ether extract was thoroughly dried over anhydrous sodium sulphate and then evaporated to dryness at 35°–40° C. The residue was weighed and then triturated with Skellysolve "F". The solution of monocarboxylic acids was reduced to about 0.5 ml. and then analyzed chromatographically by the same procedure as reported previously (8). The residual dicarboxylic acid fraction was weighed and, after the melting point and mixed melting point had been taken, analyzed chromatographically.

A typical example gave the following results: methyl oleate 74.1 mgm. (0.25 mM.) was oxidized with shaking during the course of six hours in 100 ml. solution containing 30% tertiary butanol, 25 mgm. potassium carbonate, and 20 ml. oxidant. Crude yield of saponified end products was 85.6 mgm., yielding 38.5 mgm. (97.5% of theory) monocarboxylic acid fraction and 46.7 mgm. (99% of theory) dicarboxylic acid, m.p. 104.5–106.8° C., mixed m.p. 106.2–107.3° C. with an authentic sample of azelaic acid (m.p. 106.2–107.5° C.). Chromatographic analysis gave only the bands corresponding to pelargonic and azelaic acids and their recovery was 98% (±1%).

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KINETICS OF THE OXIDATION OF URANIUM(IV) BY MOLECULAR OXYGEN IN AQUEOUS PERCHLORIC ACID SOLUTION[1]

By J. Halpern[2] and J. G. Smith

ABSTRACT

The kinetics of the oxidation of uranium(IV) by molecular oxygen in aqueous perchloric acid solution were studied. Over a considerable range of conditions, the results are fitted approximately by the rate law:
$-d[U^{IV}]/dt = k[U^{IV}]\,[O_2]/[H^+]$, where $k \approx 2\times10^{14}\exp[-22{,}000/RT]\text{sec.}^{-1}$.
The reaction is catalyzed by Cu^{++} and inhibited by small amounts of Ag^+ and Cl^-. The results are interpreted in terms of a chain reaction mechanism involving UO_2^+ and HO_2 as chain carriers.

INTRODUCTION

In recent years considerable progress has been made toward the understanding of the kinetics and mechanisms of inorganic oxidation–reduction reactions in aqueous solution (25, 10). Among the systems which have been subjected to study are those involving elementary electron transfer reactions between metal ions (25, 1), as well as reactions between metal ions and molecular oxidizing and reducing agents such as H_2O_2 (3, 24), O_2 (7), H_2 (18, 23, 12), HCOOH (2, 21, 8). The present paper reports the results of a further study of a reaction of the latter type, involving the oxidation of uranium(IV) by molecular oxygen. This reaction has been examined previously in sulphate (16) and chloride (17) solutions but the kinetics, which appeared to be fairly complex, were not fully elucidated and no conclusions were drawn concerning the reaction mechanism. The present investigation was made using perchlorate solutions, to minimize complications due to complexing between cations and anions. The question of possible intermediates in the reaction appeared to be of particular interest in view of the fact that the over-all oxidation of U^{IV} involves a net loss of two electrons while the over-all reduction of O_2 requires four electrons. A kinetic study of related interest, of the reaction between uranium(IV) and iron(III) in aqueous perchloric acid solution, has also been reported recently (4).

EXPERIMENTAL

Both Analar and Baker and Adamson perchloric acid (chloride free) were used and gave identical results. Ceric sulphate and the various perchlorate salts were obtained from G. Frederick Smith Chemical Co. All other chemicals were Baker and Adamson reagent grade. Oxygen was supplied by Canadian Liquid Air Co. Distilled water was used in the preparation of all solutions.

Solutions of uranium(IV) were prepared as follows: Hydrogen peroxide was added to a solution of uranyl nitrate (0.02 *M*) in aqueous perchloric acid

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(0.03 *M*) to precipitate uranium peroxide (this precipitation was repeated twice to ensure removal of foreign anions). The final precipitate was decomposed by boiling with dilute perchloric acid and the resulting solution of uranyl perchlorate was reduced electrolytically using a gold cathode and a platinum anode. Providing the solution was kept cold, the reduction of uranium(VI) to uranium(IV) went readily to completion.

The solutions were analyzed for uranium(IV) by titration with ceric sulphate using ferroin as indicator. To determine the total uranium content, the uranium(VI) was first reduced by passing the solution through a Jones reductor.

The glass reaction apparatus was completely immersed in a water bath whose temperature was controlled to $\pm 0.03°$ C. (most of the experiments were made at 30° C.). The oxygen gas, after saturation with water vapor, was dispersed into the reacting solution (200 ml.) through a sintered glass plate. Samples were withdrawn periodically and the concentration of unreacted uranium(IV) was measured, to determine the extent of reaction.

The oxygen partial pressure was taken as the difference between the atmospheric pressure and the vapor pressure of the solution at the reaction temperature. From the observation that the reaction rate was unaffected by variation of the oxygen flow rate in the apparatus, from 0.5 to 3 liters/min. (a flow rate of 2 liters/min. was normally used), it was concluded that the solutions were always saturated with the gas. The solution concentration of oxygen was estimated from available solubility data (19).

RESULTS AND DISCUSSION

Stoichiometry of the Reaction

With the experimental procedure that was employed, which involved passing a large excess of oxygen through the solution, there was no way of measuring the amount of oxygen which was consumed. Hence, the stoichiometry of the reaction could not be established directly. However the known chemistry of the system suggested that the only likely reaction was

$$2U^{+4} + O_2 + 2H_2O \rightarrow 2UO_2^{++} + 4H^+. \qquad [1]$$

The following observations support this stoichiometry: (1) the solutions were completely stable, and no oxidation of U^{IV} could be detected, in the absence of oxygen, (2) the titration demonstrated that oxygen converts U^{IV} quantitatively to U^{VI}, (3) spectrophotometric measurements indicated that U^{IV} and U^{VI} were the only uranium species present in the solution at any time during the reaction, (4) sensitive tests could not detect any H_2O_2 in the solution at any time during the reaction, and (5) when H_2O_2 was added to a solution of U^{IV}, it reacted instantaneously according to:

$$U^{+4} + H_2O_2 \rightarrow UO_2^{++} + 2H^+. \qquad [2]$$

These observations make it appear very unlikely that any stable products other than U^{VI} and H_2O are formed in the reaction. Hence, they support the stoichiometry represented by equation [1] which was assumed in all the subsequent kinetic work.

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Kinetics of the Reaction

Some typical rate plots, depicting the oxidation of U^{IV} in solutions containing different concentrations of $HClO_4$, are reproduced in Fig. 1. The O_2 partial pressure, and hence its concentration in solution, remained constant throughout each experiment. The change in rate during the reaction should thus reflect, principally, the changing concentration of U^{IV} in the solution.

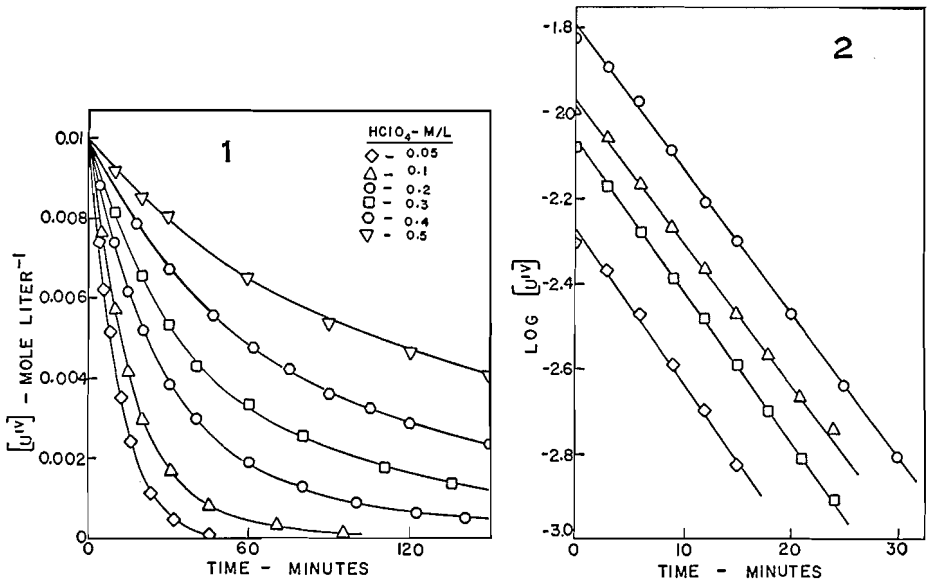

FIG. 1. Typical rate plots for the oxidation of uranium(IV) at 30° C., 0.96 atm. O_2.
FIG. 2. First-order rate plots for the reaction in solutions containing 0.08 *M* $HClO_4$ at 30° C., 0.96 atm. O_2.

At the outset it was established that the rate was unaffected by packing the reaction vessel with glass wool and by the addition of UO_2^{++} in amounts comparable to those in which it is formed during the reaction.

At relatively low $HClO_4$ concentrations (<0.2 *M*) the kinetic dependence on U^{IV} was consistently first order as shown by the plots in Fig. 2 which are fitted by the rate law:

$$-d[U^{IV}]/dt = k'[U^{IV}], \qquad [3]$$

where the apparent first-order constant, k', is independent of the initial U^{IV} concentration and of its changing concentration during the reaction.

At higher $HClO_4$ concentration, some departure from this rate law (i.e. from the linearity of the first-order rate plots) was observed, but usually not until the reaction had proceeded about halfway to completion. That this is due to some complication which develops during the course of the reaction and does not reflect an inherent departure from first-order kinetic dependence on U^{IV} is demonstrated by the fact that even at the highest $HClO_4$ concentration used (0.5 *M*), the initial slopes of the first-order rate plots (and hence the apparent

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value of k') were unaffected by varying the initial U^{IV} concentration between 0.05 and 0.15 M (see Fig. 3). Equation [3] therefore represents accurately the dependence of the initial rate on the initial U^{IV} concentration even at high $HClO_4$ concentrations. In view of this, it was decided to use the value of k' so derived (i.e. from initial slope of the first-order rate plot) as the measure of the rate in all the experiments. This seemed at least as satisfactory as adopting some more arbitrary measure of the rate, such as the time required for the completion of 50% reaction. The reproducibility of the rate measurements was about ±5% at low $HClO_4$ concentrations and ±8% at high $HClO_4$ concentrations.

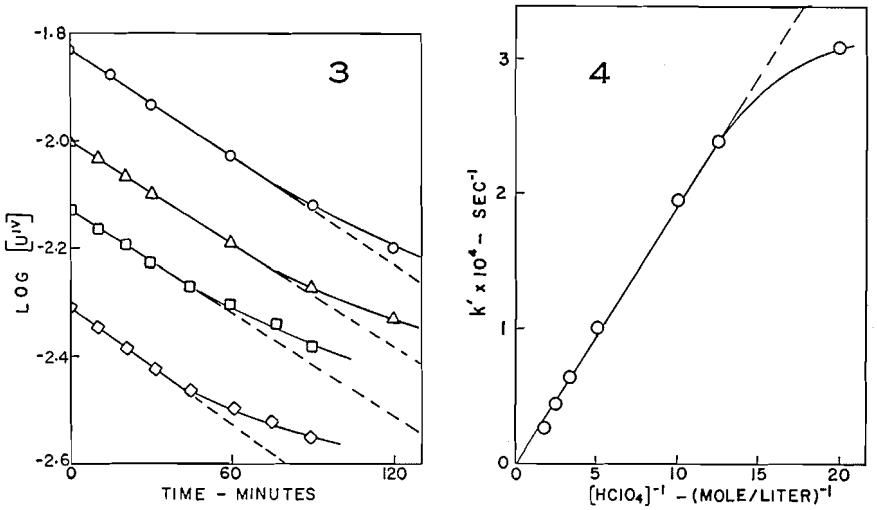

FIG. 3. Typical rate plots for the reaction in solutions containing 0.5 M $HClO_4$ at 30° C., 0.96 atm. O_2.
FIG. 4. Dependence of the rate on the concentration of $HClO_4$ at 30° C., 0.96 atm. O_2.

The reason for the apparent departure from first-order kinetics at high $HClO_4$ concentrations has not been established. It may reflect a slow secondary reaction such as hydrolysis, or the influence on the rate either of an impurity originally present in the solution or of some by-product of the reaction, which accumulates in trace concentrations as the reaction proceeds. This anomaly disappeared at higher temperatures.

The results plotted in Fig. 4 show that k' is inversely proportional to the $HClO_4$ concentration between 0.08 and 0.5 M. The simplest interpretation of this is that the U^{IV} species which takes part in the reaction is hydrolyzed. The thermodynamics of the hydrolysis reaction:

$$U^{+4} + H_2O \rightleftharpoons UOH^{+3} + H^+ \qquad [4]$$

have been determined (13) and the results indicate that at 0.5 M $HClO_4$ about 10% of the U^{IV} is present as the hydrolyzed ion, UOH^{+3}. At $HClO_4$ concentrations below 0.08 M, the inverse proportionality between k' and $[HClO_4]$ no longer applies (see Fig. 4), presumably because a relatively large proportion of the U^{IV} is hydrolyzed in this region.

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To determine the kinetic dependence on the oxygen concentration, parallel experiments were made in which air and oxygen, respectively, were passed through the solution. As shown in Fig. 5, the value of k', at both low and high $HClO_4$ concentrations, was directly proportional to the O_2 partial pressure and, hence, to the O_2 concentration in solution. Thus over a fairly wide range of conditions, the kinetics of the reaction conform approximately to the rate law:

$$-d[U^{IV}]/dt = k[U^{IV}]\,[O_2]/[H^+]\,. \qquad [5]$$

Experiments at 0.08 M and 0.5 M $HClO_4$ were made at several temperatures ranging from 20° to 60° C. The Arrhenius plots, based on values of k calculated from the slopes of first-order rate plots by means of equation [5], are shown in

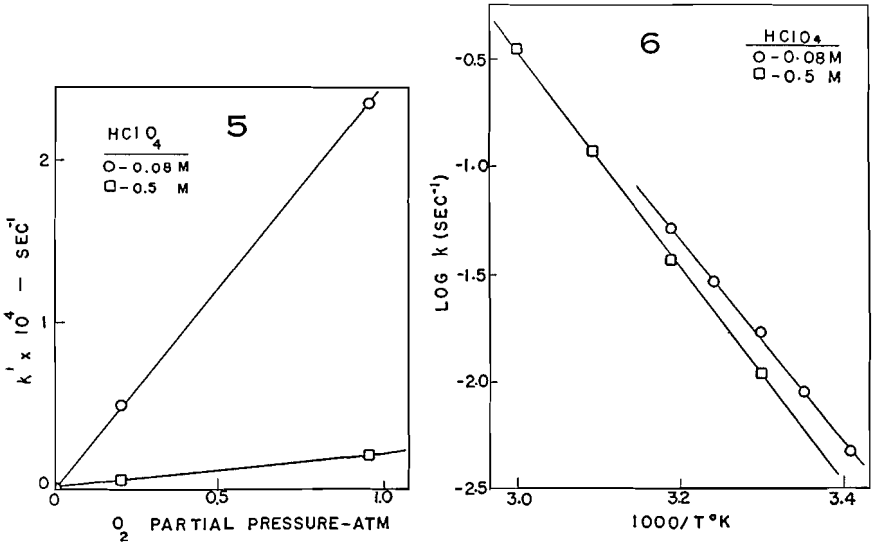

FIG. 5. Dependence of the rate on the oxygen partial pressure at 30° C.
FIG. 6. Arrhenius plots showing the dependence of the rate on temperature.

Fig. 6. The plots for the low and high acid series are seen to be displaced slightly and are fitted, respectively, by the equations:

$$k(0.08\ M\ HClO_4) = 2\times10^{14}\exp[-21{,}500/RT]\ \text{sec.}^{-1}. \qquad [6]$$

and

$$k(0.5\ M\ HClO_4) = 1.6\times10^{14}\exp[-22{,}400/RT]\ \text{sec.}^{-1}. \qquad [7]$$

The agreement between the corresponding parameters in the two equations is probably within the experimental error of the determinations. It should be noted that the apparent frequency factor in these equations is several orders of magnitude higher than would be expected for a simple bimolecular reaction, i.e. between an O_2 molecule and a hydrolyzed U^{IV} species.

Effects of Added Salts

The addition of 0.4 M Mg^{++}, 0.005 M Co^{++}, or 0.05 M Mn^{++} (all as their perchlorate salts) to solutions containing 0.5 M $HClO_4$ was found to be without

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appreciable effect on the rate. A number of other ions, including Cl^-, Ag^+, and Fe^{++}, were found to inhibit the reaction, while Hg^{++} and Cu^{++} exerted a catalytic influence. These various effects are illustrated in Fig. 7. Those due to Cu^{++}, Ag^+, and Cl^- were particularly marked and were subjected to more detailed study.

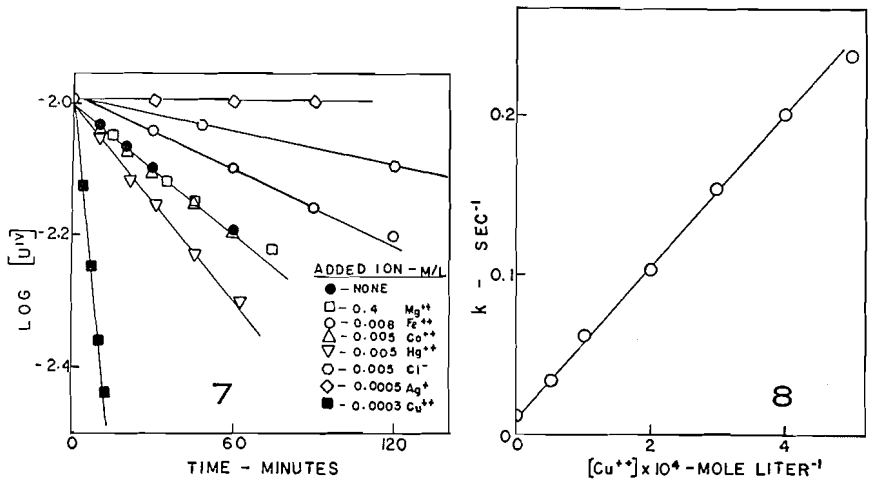

FIG. 7. Effect of various ions on the rate at 30° C., 0.96 atm. O_2, 0.5 M $HClO_4$.
FIG. 8. Dependence of the rate at 30° C. on the Cu^{++} concentration in solutions containg 0.5 M $HClO_4$.

In the presence of Cu^{++}, the rate remained first order in U^{IV}, but the apparent value of k, calculated from the slopes of the first-order rate plots, increased linearly with the Cu^{++} concentration as shown in Fig. 8. The plot in this figure is fitted by the equation:

$$k(\text{sec.}^{-1}) = 0.011 + 480[Cu^{++}] . \qquad [8]$$

The sensitivity of the reaction to Cu^{++} is very marked; thus the rate is tripled by the addition of only 5×10^{-5} M./liter of Cu^{++}. The catalytic effect of Cu^{++} on the auto-oxidation of U^{IV} has been reported previously (5, 17).

The inhibiting effect of Cl^- on the reaction is depicted in Fig. 9. Addition of only 0.001 M./liter of Cl^- (as the sodium salt) reduces the rate to about one-half its original value. It should be noted that this corresponds to only about 10% of the amount of U^{IV} originally present in the solution. Hence, the Cl^- cannot be inhibiting the reaction by tying up the U^{IV} in some inactive form (e.g. by complexing with it). Further addition of Cl^- had only a limited effect, and above 0.01 M Cl^- the rate levels off at a substantially constant value (corresponding to $k \simeq 0.002$ sec.$^{-1}$) which is about one-fifth that of the uninhibited rate.

The inhibiting effect of Ag^+ on the reaction is of quite a different form. As shown in Fig. 10, the presence of very small amounts of Ag^+ ($\simeq10^{-4}$ M./liter) was found to stop the reaction almost completely for a finite period of time, the duration of which was approximately proportional to the initial Ag^+

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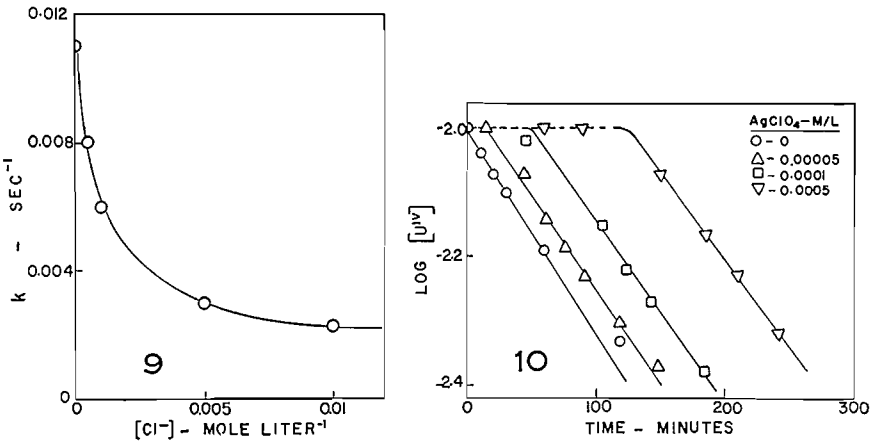

FIG. 9. Dependence of the rate at 30° C. on the Cl^- concentration in solutions containing 0.5 *M* $HClO_4$.

FIG. 10. Effect of Ag^+ on the reaction at 30° C. in solutions containing 0.5 *M* $HClO_4$.

concentration. During this interval, a gray colloidal suspension, presumably of metallic silver, was observed to form in the solution. Following the induction period, the oxidation of U^{IV} proceeded at the normal (i.e. uninhibited) rate.

CONCLUSIONS

A number of features of the kinetics, including the anomalously high frequency factor and the marked sensitivity of the rate to catalytic and inhibitory influences by various ions, strongly suggest that the reaction proceeds by a chain mechanism. The most likely intermediates would appear to be uranium(V) (generally believed to exist in solution as the UO_2^+ ion (9, 14)) and HO_2. A mechanism for the uncatalyzed–uninhibited reaction, involving these species as chain carriers, is proposed below:*

Rapid pre-equilibrium:

$$U^{4+} + H_2O \overset{K}{\rightleftharpoons} UOH^{+3} + H^+. \qquad [4]$$

Initiation step:

$$UOH^{+3} + O_2 + H_2O \xrightarrow{k_1} UO_2^+ + HO_2 + 2H^+. \qquad [9]$$

Chain propagation steps:

$$UO_2^+ + O_2 + H_2O \xrightarrow{k_2} UO_2^{++} + HO_2 + OH^-, \qquad [10]$$

$$HO_2 + UOH^{3+} + H_2O \xrightarrow{k_3} UO_2^+ + H_2O_2 + 2H^+. \qquad [11]$$

Termination step:

$$UO_2^+ + HO_2 + H_2O \xrightarrow{k_4} UO_2^{++} + H_2O_2 + OH^-. \qquad [12]$$

Fast reaction:

$$U^{+4} + H_2O_2 \rightarrow UO_2^{++} + 2H^+. \qquad [2]$$

**The reactions included in the proposed mechanism were selected because they appear reasonable on chemical and energetic grounds and because they form a sequence which is compatible with the observed kinetics However the available evidence does not rule out the possibility that other reactions also participate. For example the referee has pointed out that the disproportionation of* UO_2^+, *i.e.*

$$2UO_2^+ + 4H^+ \rightarrow UO_2^{++} + U^{++++} + H_2O,$$

may compete with the suggested termination step, represented by equation [12], particularly at high acidities. This seems plausible in the light of available kinetic (9) and thermodynamic (15) data about this reaction.

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K is the equilibrium constant for the initial step, while k_1, k_2, k_3, and k_4 are the respective rate constants for the initiation, propagation, and termination steps.

Using the steady-state method, the following rate law has been derived for this mechanism:

$$-d[U^{IV}]/dt = 2k_1K\{1+(k_2k_3/k_1k_4)^{\frac{1}{2}}\}[U^{4+}]\,[O_2]/[H^+]\,. \qquad [13]$$

This has the same form as equation [5] and is thus qualitatively consistent with the experimental results.

The marked catalytic influence of Cu^{++} may be explained through the following reactions* which generate UO_2^+ and HO_2 and thus cause chain initiation:

$$Cu^{++} + UOH^{+3} + H_2O \rightarrow Cu^+ + UO_2^+ + 3H^+, \qquad [14]$$

$$Cu^+ + O_2 + H^+ \rightarrow Cu^{++} + HO_2. \qquad [15]$$

The inhibiting effect of Cl^- can be accounted for by reactions between Cl^- and the chain-carrying species, UO_2^+ and HO_2, which result in disruption of the chain, i.e.

$$UO_2^+ + Cl^- + 2H_2O \rightarrow UOH^{+3} + Cl + 3OH^-, \qquad [16]$$

$$HO_2 + Cl^- + H_2O \rightarrow H_2O_2 + Cl + OH^-, \qquad [17]$$

$$UO_2^+ + Cl \rightarrow UO_2^{++} + Cl^-, \qquad [18]$$

$$HO_2 + Cl \rightarrow O_2 + Cl^- + H^+. \qquad [19]$$

The last two reactions also result in the regeneration of Cl^- and, hence, in the indefinite persistence of the inhibition.

A similar explanation can be advanced for the inhibition due to Ag^+, which can disrupt the chain through the following reactions:

$$UO_2^+ + Ag^+ \rightarrow UO_2^{++} + Ag, \qquad [20]$$

$$HO_2 + Ag^+ \rightarrow O_2 + H^+ + Ag. \qquad [21]$$

However in contrast to Cl^-, the Ag^+ is apparently removed irreversibly from the solution (i.e. as metallic silver) as a result of these reactions. Hence its inhibiting effect persists only for a limited time, following which the reaction proceeds normally.

The influence of other catalysts and inhibitors (e.g. Hg^{++} and Fe^{++}), all of which are readily oxidizable or reducible ions, can be accounted for through similar reactions.

A number of other examples have been recorded of inorganic oxidation–reduction reactions which proceed through chain mechanisms, analogous to that which has been proposed for the present system, and whose rates are susceptible to similar catalytic and inhibitory influences (3, 24, 22, 11, 20, 6). Some of these reactions involve O_2 as the oxidant. However, this appears to be the first time that a chain reaction in aqueous solution, involving a uranium species as the chain carrier, has been reported.

**Reaction [15] seems plausible on energetic grounds (15), although the reverse of this reaction has also been postulated to occur (e.g. Reference 4) under certain conditions.*

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ACKNOWLEDGMENT

We are grateful to Dr. R. H. Betts for helpful discussion about this reaction and for making available to us his unpublished data on it.

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THE SYSTEMS ALUMINUM-TIN AND ALUMINUM-LEAD-TIN[1]

By A. N. Campbell and R. Kartzmark[2]

ABSTRACT

The solubility of tin in aluminum, between 400° and 645° C., has been determined by an isothermal method. The system Al–Pb–Sn has been investigated, isothermally, at 500° and 600° C. The eutectic temperature and composition of this system have also been determined. The structure of the phases in completely solid alloys has been identified by photomicrography. The liquidus curves at 500° and 600° C. are continuous, extending across the ternary diagram from the Al–Pb system to the Al–Sn system. On neither of the two isotherms does a two-liquid region occur, despite the fact that a well-defined two-liquid region exists at temperatures above 650° C. This was found to be due to inaccuracy in the published diagram for the Al–Sn system and this led to the work mentioned above. The solubility of tin in aluminum is much less than it has been supposed and this causes the surface of solid aluminum to intrude into the solid diagram at an early stage, thus blocking out the two-liquid region. The ternary eutectic temperature is 183.0° C. and the composition, 0.08 weight per cent Al, 38.1% Pb, and 61.7% Sn. In any alloy at room temperature, the solid phases are: primary aluminum, α-lead, and β-tin. Brinell Ball and Vickers Diamond Pyramid hardness tests show that the ternary eutectic alloy is the hardest of the system. When alloys approximating to the eutectic composition are used as solders, it has been found that the alloy of ternary eutectic composition has a greater shear strength than ordinary solder.

Despite the simplicity of the three-component system, Al–Pb–Sn, it has not been studied previously in its entirety; work has been confined to the completely liquid two-layer condition. Wright (10), working between 750 and 850° C., found the critical solution to contain 64 weight per cent tin and 17% lead. Lorenz and Erbe (4) carried out a few experiments at 750° C., using a quenching technique, but their results are too crude to merit mention. Very excellent work was done by Davies (2) in 1953. He studied the region of partial miscibility at 650°, 730°, and 800° C., using the purest materials and keeping the temperature truly constant. Davies' data are shown graphically in Fig. 1. It is surprising that the numerical values were never published. We consider these data so valuable that we offer them here, with the consent of the author.

Of the component binary systems, little need be said of the systems Al–Pb and Pb–Sn, save that they are simple and have been investigated completely. The system Al–Pb gives at all temperatures above 658.5° C. two liquid layers; in the solid state there is no compound formation or appreciable solid solution (11).

The Pb–Sn system, to which the soft solders belong, exhibits a simple eutectic accompanied by considerable solid solubility of tin in lead, at the eutectic temperature of 183.3° C., but this decreases to zero at room temperature (6). The lead-rich alloys show a mysterious evolution of heat, on cooling, at about 150° C., and for this no satisfactory explanation has been offered, though the fact is beyond question.

[1]*Manuscript received May 28, 1956.*
Contribution from the Chemistry Department, University of Manitoba, Winnipeg, Manitoba.
[2]*Holder of the Cominco Fellowship, University of Manitoba, 1955–56.*

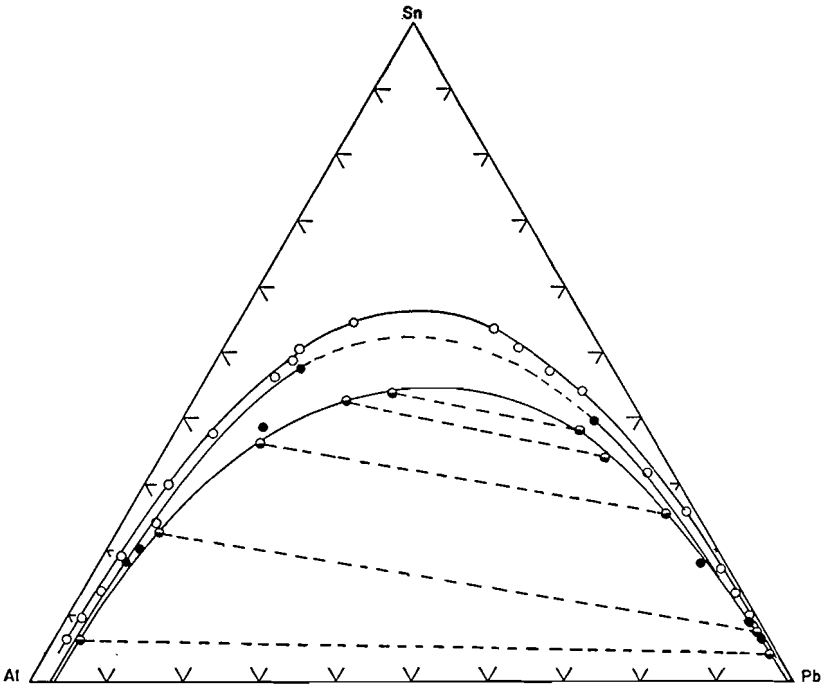

FIG. 1. The liquid immiscibility region in the aluminum–lead–tin system at 650° (○), 730° (●), and 800° C. (◑). (Davies)

The remaining binary system, Al–Sn, is also simple in character (3). Some earlier claims for the existence of an intermetallic compound, AlSn, have now been given up. It is probable that the distorted (non-ideal) form of the liquidus gave rise to these claims. It was the distorted character of the liquidus which led to our redetermining it. Between 10 and 90 weight per cent aluminum, the liquidus is almost horizontal; to be exact, the equilibrium temperature changes only by about 100° over this region, i.e. about 1° per 1%. It results from this that determination of the form of the liquidus by thermal analysis, the method invariably used hitherto, is bound to give low results in respect of temperature. If the accepted curve is too low in respect of temperature, it results from this that if this curve is used to interpret a temperature in terms of composition, the aluminum content appears too high. Our work on the ternary system Al–Pb–Sn convinced us that this was the case and led to our redetermination of part of the Al–Sn liquidus by an isothermal method.

EXPERIMENTAL

It is unnecessary, in these days of pure materials, to give lengthy analyses of trace elements. Suffice it to say that the aluminum was a special research grade kindly donated to us by the Aluminum Company of America, the lead was Merck 'Reagent' grade, and the tin (so-called 'commercial', from the Vulcan Detinning Company) was actually a very pure product, containing 99.995% tin.

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TABLE I

RESULTS OF M. H. DAVIES ON THE AL–PB–SN SYSTEM
Al-rich in equilibrium with Pb/Sn-rich

Al	Pb	Sn	Al	Pb	Sn
		At 650° C.			
92.0	1.7	6.3	0.3	94.3	5.3
88.3	2.0	9.7	0.3	92.7	7.0
84.0	2.3	13.7	0.7	89.3	10.0
78.7	2.3	19.0	1.0	85.7	13.3
71.7	4.3	24.0	1.0	82.0	17.0
67.0	3.0	29.7	1.3	73.0	25.7
57.3	5.0	37.7	3.7	66.0	31.7
45.0	9.0	46.0	5.7	50.3	44.0
41.3	10.0	48.7	8.3	44.6	47.0
39.7	10.0	50.3	10.7	38.7	50.7
30.7	15.0	54.3	12.6	34.0	53.7
		At 730° C.			
78.7	3.3	18.0	1.0	92.6	6.7
75.7	4.3	20.0	1.0	90.3	9.0
50.3	11.0	38.7	3.3	69.0	27.7
41.0	11.6	47.3	6.3	54.3	39.3
		At 800° C.			
90.7	3.3	6.0	1.0	95.3	3.7
72.0	5.3	22.7	1.0	91.7	7.3
No analysis for sample			1.3	87.0	11.7
52.0	12.0	36.0	4.0	70.6	25.0
37.3	20.0	42.7	7.7	58.3	34.0
35.7	20.7	43.7	9.0	53.0	37.0

NOTE: *These results are taken from the analysis of 150 samples and are adjusted to the nearest ⅓%. At low concentrations only the minor constituents were analyzed but at higher concentrations figures for lead, tin, and aluminum were obtained. Total errors amounting to 2% were common in the latter case and in isolated samples the total error was occasionally as high as 5%.*

Because of the ready oxidation, in the furnace, of all three metals, the composition of all alloys had to be determined by chemical analysis. After trying in vain to adopt polarographic and conductometric methods, we finally used the following method which, though old-fashioned and crude, was sufficiently accurate for our purposes. Tin was determined as metastannic acid, ignited to SnO_2. The filtrate was diluted to known volume and aliquot portions used for lead and aluminum determination. Lead was estimated as chromate, weighed on a sintered glass crucible. Aluminum was determined as hydroxyquinolate, in the presence of lead. Determination of aluminum in lead–aluminum mixtures of known composition showed that lead did not interfere. When the alloy contained less than two per cent aluminum, the hydroxyquinolate was dissolved in hydrochloric acid and reprecipitated.

It has been the practice of this laboratory, for some years past, to make increasing use of the isothermal method, rather than that of thermal analysis, for the determination of liquidus curves and surfaces. In effect, this amounts to taking horizontal sections of the three-dimensional model and, in our opinion, the method is often more accurate than that of thermal analysis although, of course, thermal analysis will always retain its value.

The method of keeping the furnace at constant temperature is essentially

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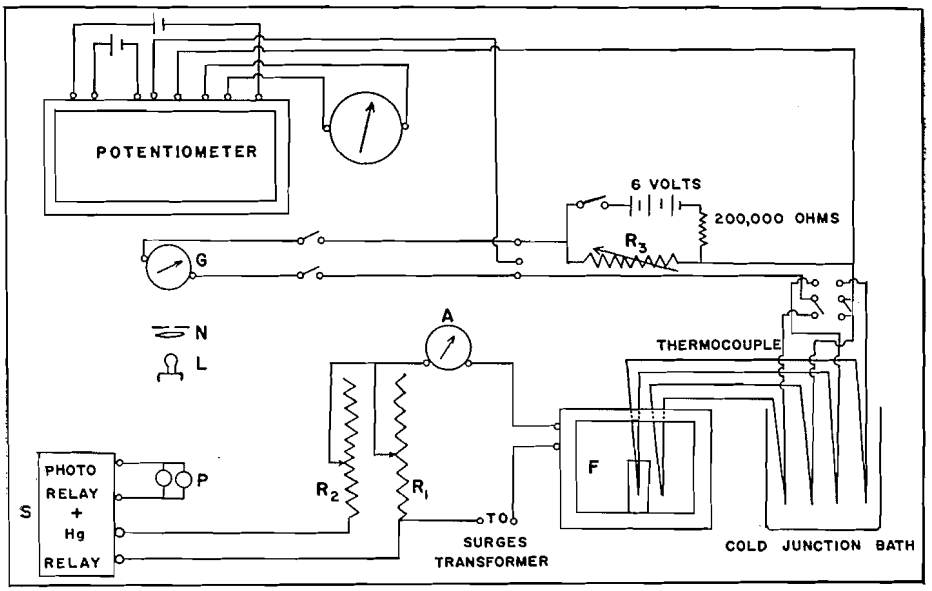

FIG. 2. Temperature control circuit.

that of Lutz and Wood (5) but the circuit is now much simplified. The essential layout is shown in Fig. 2. The furnace, F, contains two chromel–alumel thermocouples, one actually in the melt, the other in the air space of the furnace. Either of these thermocouples can be switched into the potentiometer circuit when it is desired to measure temperature. A constant current from the transformer to the furnace, through resistance R_1, is sufficient to keep the furnace a few degrees below the desired temperature. A second resistance, R_2, in parallel with R_1, supplies additional current under control. It was found that the additional current had to be reduced to a few tenths of an ampere for good temperature control. Control is obtained by opposing the thermocouple e.m.f. by an equal e.m.f., obtained by applying a potential divider to a 6-volt storage battery. This circuit also contains a delicate galvanometer. When the thermocouple e.m.f. exceeds the opposing e.m.f., the mirror of the galvanometer moves, reflecting a spot of light onto the photocells. These cells then operate the relay, cutting out the extra heating current. Simple as the arrangement is, it operates admirably for our purposes, giving a constancy of $\pm 0.5°$, at 600° C. The thermocouples were calibrated by means of pure tin, lead, zinc, and aluminum. The thermocouple in the melt gave the actual temperature of the melt, while the other served to keep the furnace under control while the former thermocouple was removed for sampling of the melt. Most alloys had a crust of solid aluminum on the top and the hole left by removal of the thermocouple case served for sampling.

Alundum ware (crucibles, sampling tubes, thermocouple case, etc.) was used throughout: glass is rapidly reduced by hot aluminum, with production of elementary silicon.

All isotherms were determined at temperatures below the freezing point of aluminum and therefore aluminum was always a solid phase. To ensure

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homogeneity of the liquid phase, all alloys were heated to complete fusion with stirring, before their introduction to the furnace. The alloy was then allowed to cool in the furnace, with constant stirring with an alundum rod, until the controlled temperature was reached. The alloy was then kept at controlled temperature for from 4 to 24 hr., before a sample was withdrawn for analysis. Sampling was done by withdrawing molten alloy through a narrow ($\frac{1}{16}$ in. inside diameter) alundum tube. The alloy solidified in the tube just above furnace height. The entire sample was weighed and analyzed; this was done in case there had been segregation of the sample in the tube. We satisfied ourselves by frequent sampling of top and bottom of crucible contents that two liquid layers never occurred at the temperature of investigation.

The ternary eutectic temperature and composition in the Al–Pb–Sn system were determined by thermal analysis. Aluminum was added in very small quantities at a time to the binary eutectic mixture of the Pb–Sn system until the eutectic temperature remained constant. The eutectic alloy was then analyzed.

The techniques of polishing and of photomicrography are well known. The polishing and etching of these soft metals is, however, notoriously difficult. We used as etching reagent that of Villela and Beregekoff (9); it consists of a mixture of glacial acetic acid, nitric acid, and glycerol. The results were extremely satisfactory, as can be seen from our photomicrographs.

Hardness was determined by means of a modified Brinell tester (load 5.5 kgm.) and by the Vickers-Armstrong tester. To test the tensile strength, the alloys were treated as solders, in the following manner: Two pieces of half-inch brass strip, six inches long, were soldered together in the form of a lap joint; the area of the lap was one-eighth of a square inch. Both pieces were 'tinned' with the solder under investigation, then fused together. Any excess of solder round the joint was removed with a file. The strength of the joint was determined with an Olsen 10,000 lb. tester. Four tests were made with each solder and the results, which agreed reasonably well, were averaged.

EXPERIMENTAL RESULTS

TABLE II

SOLUBILITY OF ALUMINUM IN TIN BETWEEN 400° AND 645° C.

Alloy No.	Temperature, ° C.	Composition by weight	
		Al	Sn
1	400	2.6	97.5
2	425	3.3	97.0
3	450	4.0	96.0
4	475	4.8	95.2
5	500	5.4	94.6
5*a*	500	5.7	93.9
6	525	8.3	92.1
7	550	11.8	88.3
8	575	17.1	83.0
9	600	30.8	69.1
9*a*	600	29.9	68.8
10	625	58.6	41.0
11	645	87.6	12.4

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TABLE III

COMPOSITION OF LIQUIDUS IN EQUILIBRIUM WITH SOLID ALUMINUM AT 500° C., IN SYSTEM AL–PB–SN

Alloy No.	Al, wt. %	Pb, wt. %	Sn, wt. %
2	3.5	27.5	69.1
3	4.0	16.1	80.0
4	4.9	6.2	88.8
5	5.7	0.0	93.9
5*a*	5.5	0.0	94.4

TABLE IV

COMPOSITION OF LIQUIDUS IN EQUILIBRIUM WITH SOLID ALUMINUM AT 600° C. IN SYSTEM AL–PB–SN

	Composition by weight		
Alloy No.	Al	Pb	Sn
6	5.0	43.0	52.5
9	9.1	30.4	60.5
10	10.3	26.2	63.5
11	0.45	85.0	15.1
12	29.2	0.0	68.8
12*a*	30.3	0.0	68.9
13	2.7	61.3	36.5
14	5.5	40.2	54.5
15	9.4	27.7	63.1
16	15.9	12.2	70.5
17	23.8	5.2	71.4

TABLE V

COMPARISON OF PB–SN EUTECTIC WITH AL-PB-SN EUTECTIC

		Composition of liquid (wt. %)		
Eutectic	Temperature, ° C.	Al	Pb	Sn
Pb–Sn	183.3	—	38.1	61.9
Al–Pb–Sn	183.0	0.08	38.1	61.7

The results of Table II are plotted as the equilibrium diagram Fig. 3. Experiments were not carried below 400° C. because below that temperature our results were in agreement with the published results, and, in any case, the solubility is too small to be interesting. The dotted curve of Fig. 3 represents ideal behavior as calculated by Seltz' (7) thermodynamic equations. The difference between the dotted and full curves points up the very non-ideal form of the liquidus.

Fig. 4 is the equilibrium diagram of the system Al–Pb–Sn at 500° C., derived from the data of Table III; in all cases aluminum was the solid phase. The investigation was not pursued below 69% tin content, since the aluminum

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TABLE VI

SOME MECHANICAL PROPERTIES OF THE PURE METALS AND CERTAIN ALLOYS OF THE SYSTEM AL–PB–SN

Alloy	Hardness		Tensile strength as a solder, p.s.i.
	B.h.n.*	D.P.H.†	
Al	14.9	16.6	——
Sn	5.0	11.4	——
Pb	3.4	7.6	——
Pb–Sn eut.	14.2	16.4	6200
Al–Pb–Sn eut.	18.2	19.8	6450
Pb–Sn eut. + 1% Al	15.8	18.4	5900
Pb–Sn eut. + 5% Al	14.2	17.7	——

The shear strength of a soldered joint under prolonged load was determined for the Pb–Sn eutectic. This solder supported 1360 p.s.i. for 264 hr. at room temperature.

**Diameter of ball, 2.5 mm.; load, 5.5 kgm.; time of application, 30 sec.*

†*Load, 5.0 kgm.*

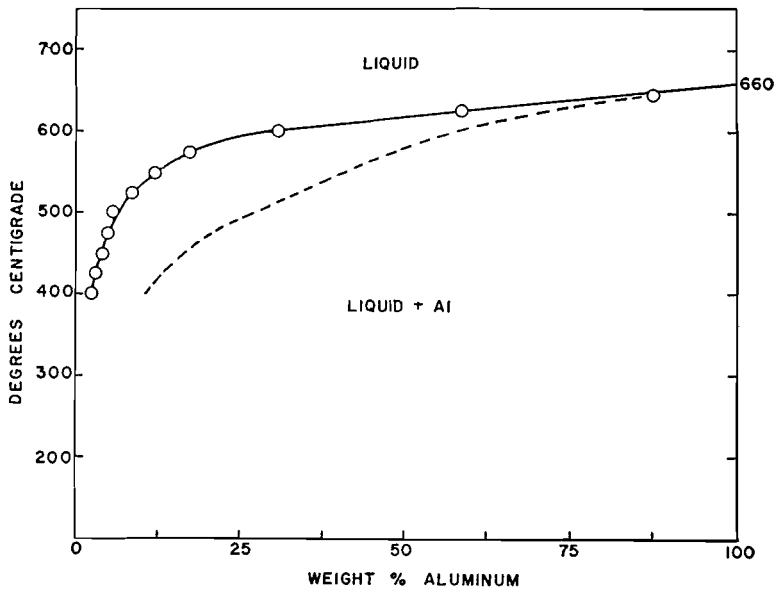

FIG. 3. System aluminum–tin. Equilibrium diagram.

content had fallen to 3.5% and since the solubility of aluminum in lead, at 500° C., is only 0.02% (1). Fig. 5 is the corresponding isotherm for 600° C. Even at 600° C., no two liquid layers were ever observed.

Figs. 6–11 are photomicrographs (×500) showing the various phases in equilibrium, in the region of the ternary eutectic.

Table VI shows the relationship between the hardness of the pure metals, the Pb–Sn eutectic, and two alloys having primary separated aluminum. Brinell Ball and Vickers Diamond Pyramid hardness numbers are given. The trend in the hardness is the same on both scales. The binary eutectic alloy was

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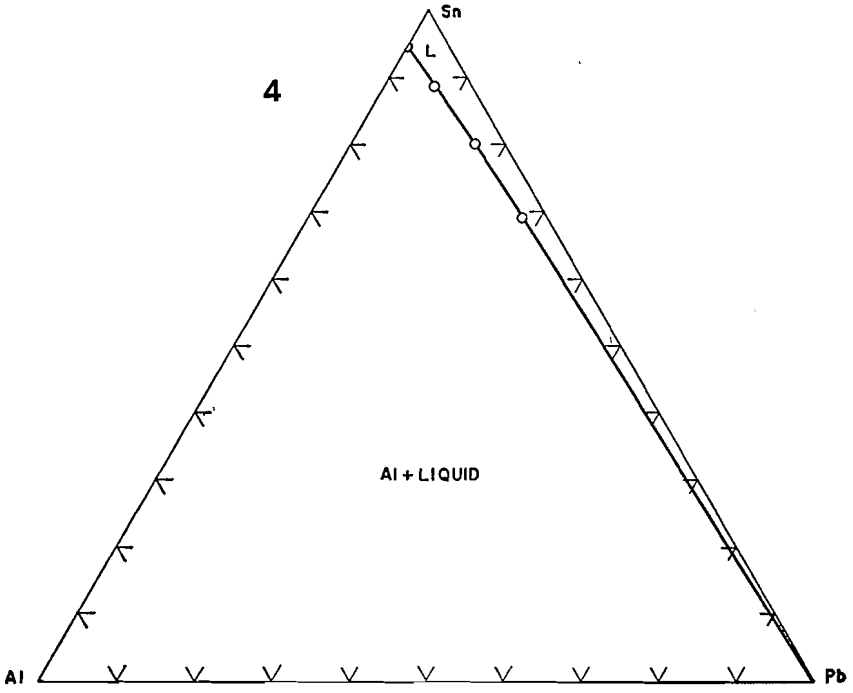

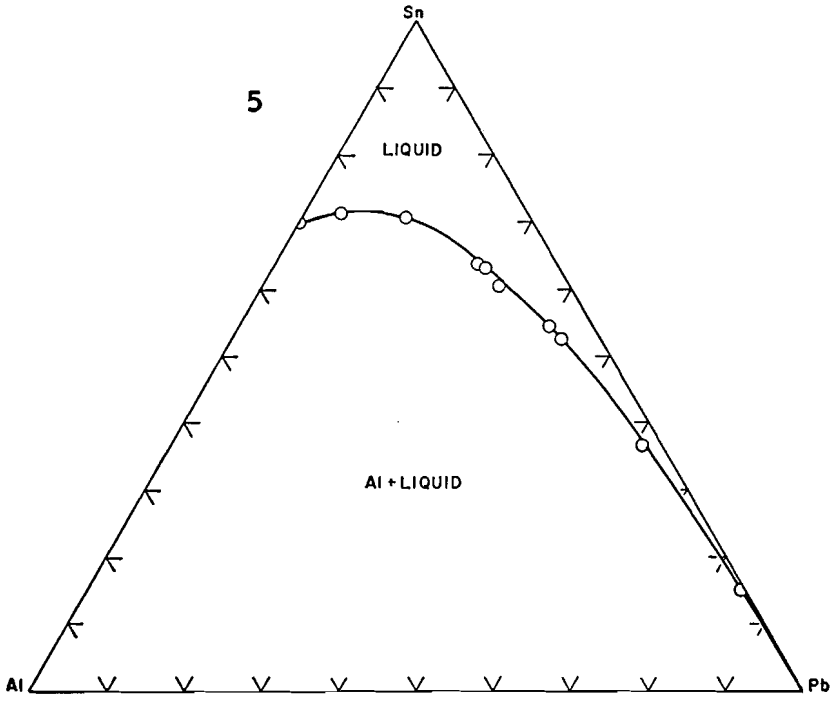

FIG. 4. 500° C. isotherm system Al–Pb–Sn.
FIG. 5. 600° C. isotherm system Al–Pb–Sn.

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found to have a greater hardness than lead or tin, the two pure components. Likewise the ternary eutectic alloy had a greater hardness than both the binary Pb–Sn eutectic and aluminum, the third alloying component. The alloy made by adding 1% aluminum to the Pb–Sn eutectic, thus forming an alloy that was mainly ternary eutectic surrounding primary separated aluminum, had a hardness less than the eutectic and approaching that of pure aluminum. Aluminum occupies about 20% of the volume in the alloy containing 5 weight per cent aluminum plus the Pb–Sn eutectic composition. Consequently the hardness of this alloy was almost equal to that of pure aluminum.

The effect of aluminum on the shear strength of the Pb–Sn eutectic solder was determined. As shown in Table VI the shear strength and the hardness were greater for the ternary eutectic than for the binary. The alloy containing 1% aluminum showed a marked decrease in shear strength due to the appearance of primary aluminum. The 5% aluminum alloy could not be used as a solder owing to the large volume of aluminum present. Aluminum does not fuse at soldering temperatures.

DISCUSSION OF RESULTS

When this work was commenced it was naturally supposed that the region of solid aluminum would intrude, with falling temperature, into the region of two liquid layers, giving rise to an invariant triangle, i.e. a heterogeneous area in which solid aluminum is in equilibrium with two liquid layers of fixed composition; further addition of tin would cause solid aluminum to disappear and a region of two congruent liquids to appear, terminating in a liquid of critical composition. In fact, however, no congruent triangle or two-liquid region was observed, either at 500° or at 600° C. Phenomena as described above must exist somewhere between 600° C. and the melting point of aluminum but, since this represents an extreme range of 60°, it was not thought worth while to pursue the matter further. The interesting thing is the absence of a two-liquid region at 600° C., for the figures of Davies (2) on the two-liquid region, at and above 650° C., and the accepted equilibrium diagram of the system Al–Sn would certainly lead one to expect the existence of a two-liquid region at 600° C. We were hence forced to the conclusion that the accepted solubility figures of aluminum in tin were erroneous and this led to our redetermining part of this diagram. We have plotted our results for Al–Sn, along with those of Sully, Hardy, and Heal (8), the latest and presumably the best work, in Fig. 12; the dotted line represents the results of Sully, Hardy, and Heal. The two curves coincide between 400° and 450° C., and between 450° and 550° C. the deviation in composition is less than two per cent by weight. Above 550° C., the curve flattens out and, although the difference in temperature between the two curves is only about 10° C., in this region, the difference in composition can be as great as 20%. Sully, Hardy, and Heal used thermal analysis and this method does not yield accurate results when there is a large change in composition for a small change in temperature.

Using our new data, for the solubility of aluminum in tin, it became obvious that a two-liquid region is no longer to be expected at 600° C.; the miscibility

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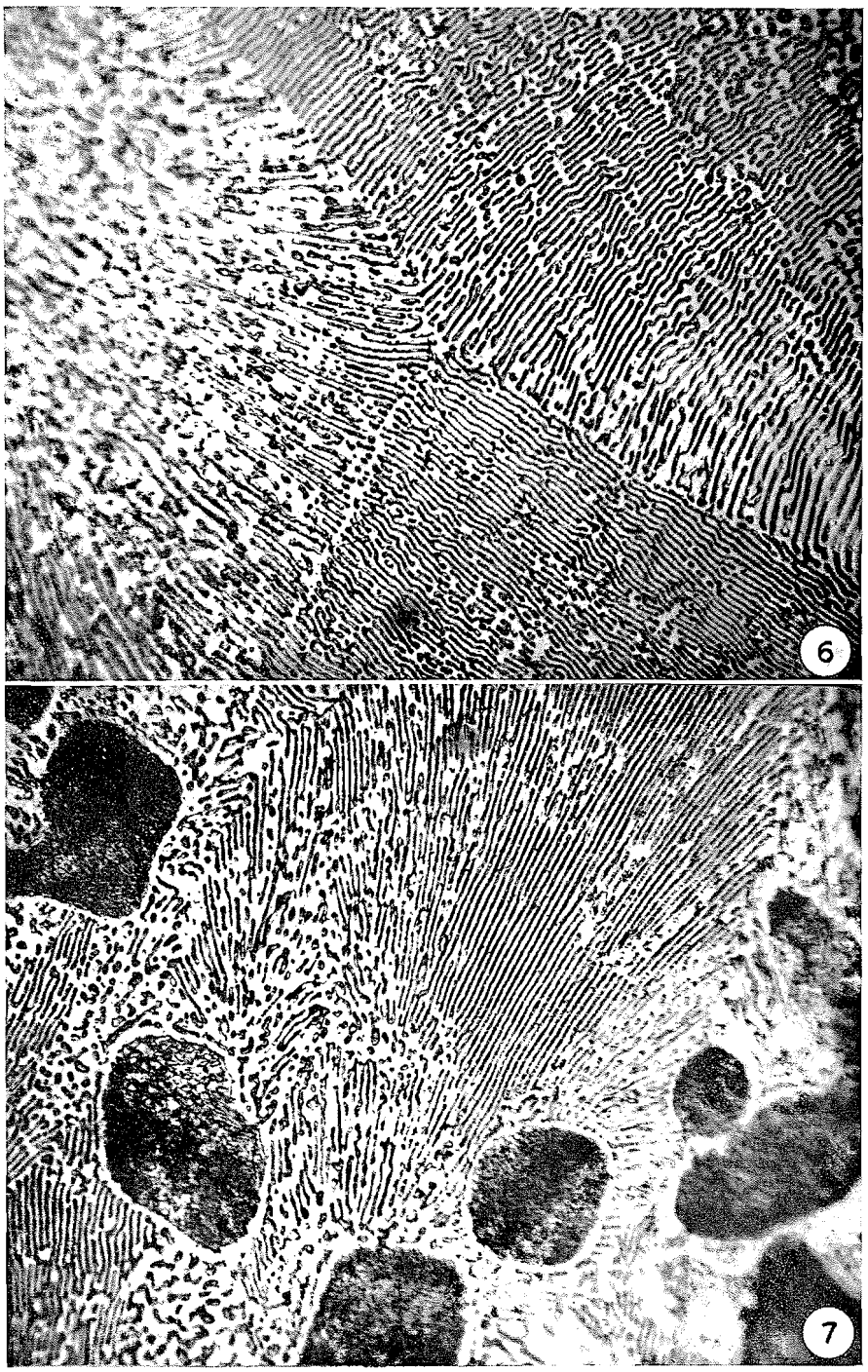

FIG. 6. Pb–Sn eutectic, ×500.
FIG. 7. Alpha lead embedded in Pb–Sn eutectic matrix, ×500.

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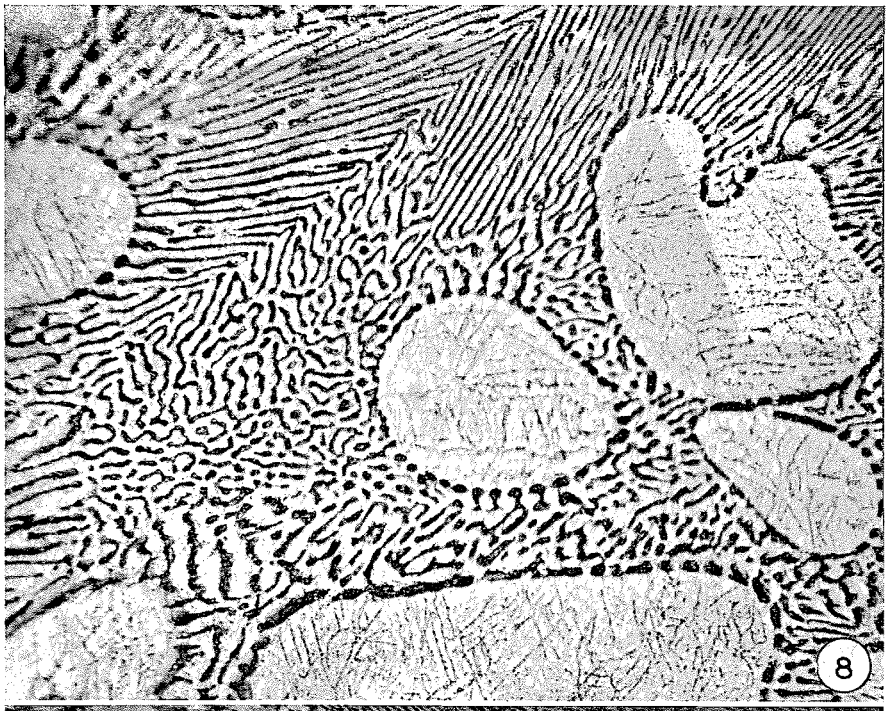

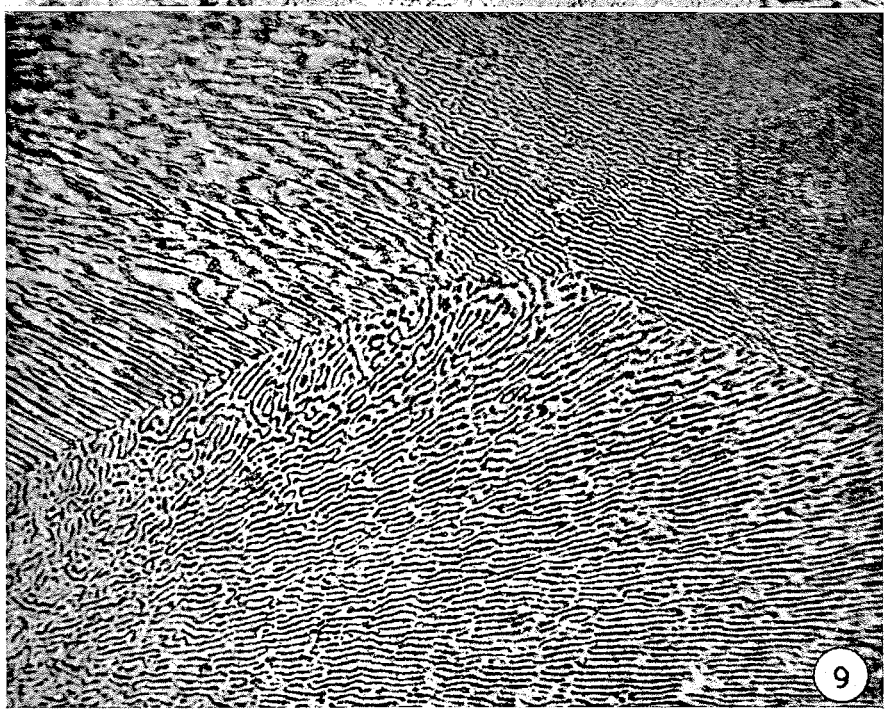

FIG. 8. Beta tin embedded in Al–Pb–Sn eutectic matrix, ×500.
FIG. 9. Al–Pb–Sn eutectic, ×500.

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FIG. 10. Primary aluminum in Al–Pb–Sn eutectic matrix, ×500.
FIG. 11. Alpha lead (dark), primary aluminum (light) in Al–Pb–Sn eutectic matrix, ×500.

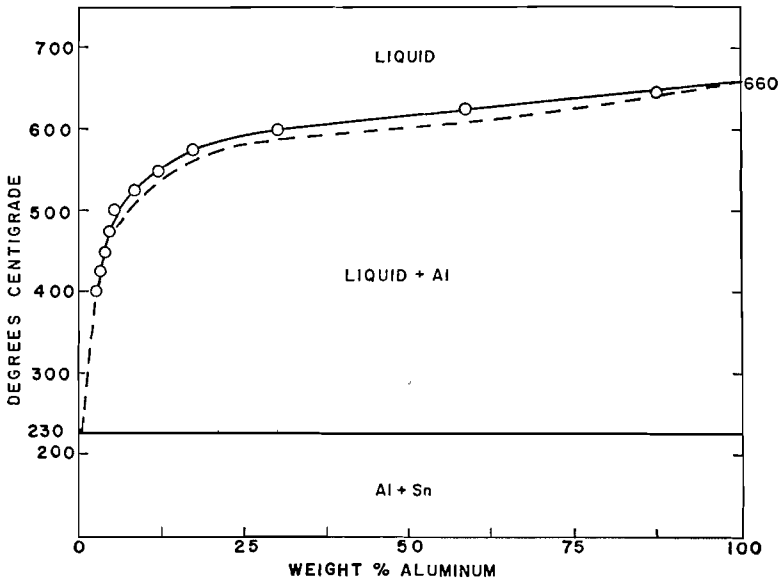

FIG. 12. System aluminum–tin. Redetermined equilibrium diagram.

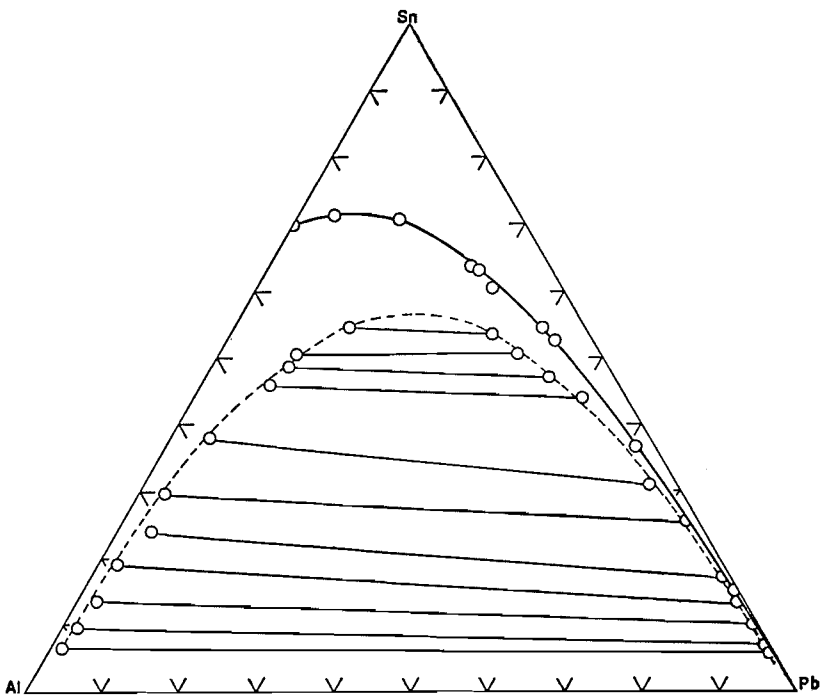

FIG. 13. System Al–Pb–Sn. ——— 600° C. isotherm. - - - - - - 650° C. isotherm.

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gap which undoubtedly exists at 650° C. (Davies (2)) is completely intruded by solid aluminum at 600° C. This is illustrated in Fig. 13 which shows our 600° isotherm and that of Davies for 650° C. The diagram shows to what extent the region of solid aluminum has moved across the region of two liquids, when the temperature has dropped 50°.

The ternary eutectic is very near to the binary eutectic of the Pb–Sn system. The binary eutectics of the Al–Pb and the Al–Sn systems contain very little aluminum and therefore the eutectic troughs must almost coincide with the side of the diagram; in other words, the amount of aluminum in any eutectic of the system is almost vanishingly small.

The photomicrographs are almost self-explanatory and are only of interest as being unusually fine examples of photomicrographs of soft metals. Figs. 6 and 9 show the lamellar structure of the Pb–Sn and Al–Pb–Sn eutectics respectively. Fig. 7 shows α-lead embedded in Pb–Sn eutectic matrix. The solubility of tin in lead at the eutectic temperature is 19.2%, while at room temperature it is only $1\frac{1}{2}$%. The α-phase exhibits a white outline and light spots, owing to the precipitation of tin in the solid phase as the temperature is lowered.

Fig. 8 is a photomicrograph of a ternary alloy that has been allowed to solidify in the furnace, then thrust into powdered dry ice for quenching. It shows β-tin embedded in eutectic matrix. Tin contains 2.5% lead in solid solution at the eutectic temperature but only a negligible amount at room temperature. The β-phase here shows lead precipitated at the grain boundaries and in the crystallographic planes. This structure is called widmannstätten. The central island exhibits an example of twinning through cold working.

Primary separation of aluminum in an Al–Pb–Sn matrix is shown in Fig. 10. The sample was selected so that the outside edge of the ingot formed one side of the specimen. One of the sides perpendicular to this edge was then polished and etched. This alloy contained 1% aluminum and lead and tin in the eutectic ratio and shows a primary aluminum crystal formed at the outer edge of the ingot. The phases present in an alloy containing 5% aluminum plus the Pb–Sn eutectic are shown in Fig. 11. α-Lead is the dark phase with some tin precipitated. The light polygonal-shaped crystallites are primary aluminum. Because aluminum is more resistant to the polishing abrasive, these crystallites are not in the same plane as the α-lead and eutectic matrix, and hence are slightly out of focus.

ACKNOWLEDGMENT

In this, as in all similar work, we acknowledge our deep indebtedness to Professor C. M. Hovey, of the Department of Civil Engineering, without whose patient supervision the photomicrographs would be impossible.

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A CONVENIENT SYNTHESIS OF DL-GLUTAMIC ACID FROM β-PROPIOLACTONE[1]

By Guy Talbot, Roger Gaudry, and Louis Berlinguet

ABSTRACT

A new synthesis of DL-glutamic acid was carried out in an over-all yield of 87% from condensation between β-propiolactone and the sodium salt of diethyl acetamidomalonate, followed by acid hydrolysis. When desired, the intermediate product, the diethyl ester of N-acetyl-2-carbethoxyglutamic acid, could be isolated in a 68% yield and hydrolyzed to glutamic acid via the hydrochloride in a 95% yield.

INTRODUCTION

L-Glutamic acid is a natural α-aminodicarboxylic acid obtainable by hydrolysis of many albumins and particularly of gluten from which it was isolated for the first time (20). Numerous syntheses of racemic glutamic acid have been published since and according to the methods of preparation, they can be divided into three main groups: (1) Syntheses involving a reduction step on either α-oximinoglutaric acid, α-diazoglutaric acid, or α-oxoglutaric acid and their esters (23, 13, 7, 3, 12, 10, 21, 15). (2) The Strecker reaction performed on β-aldehydopropionic acid (9, 2). (3) Condensation of diethyl malonate derivatives with various compounds (8, 4, 19, 14, 22, 1, 6). Another method was recently published by Paris *et al.* (18) starting from γ-butyrolactone.

Of these preparations, few are of practical interest. The best ones involve condensation of a malonic acid derivative with methyl acrylate (14, 22) or acrylonitrile (1, 6).

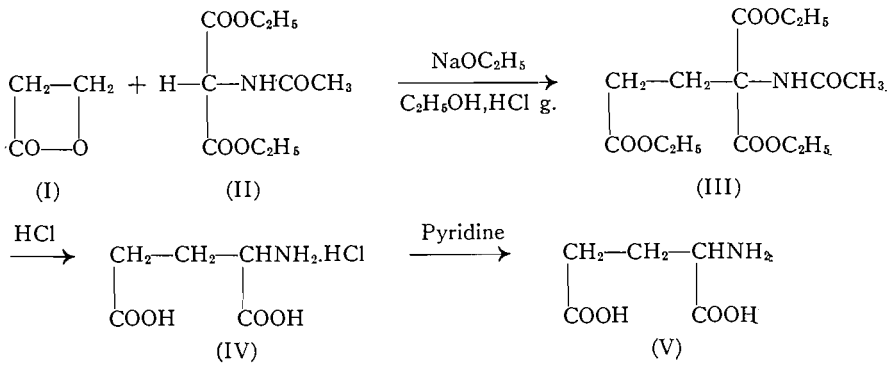
We have investigated the preparation of DL-glutamic acid from the commercially available β-propiolactone (11) and diethyl acetamidomalonate. The chemistry of β-lactones has been recently reviewed by Zaugg (24). According to the general expectations, whenever β-propiolactone reacts with a compound MX in the ionized form, the cleavage should occur at the alkyl–oxygen bond.

Advantage was taken of that property and β-propiolactone (I) was condensed at 0° C. with the sodium salt of diethyl acetamidomalonate (II) in absolute ethanol.

The one-step reaction including condensation of (I) with (II) and immediate hydrolysis, without isolation of any intermediate, gave an 87% yield of glutamic acid (V).

The intermediate compound, the diethyl ester of N-acetyl-2-carbethoxyglutamic acid (III), has been isolated in a 68% yield and transformed to glutamic acid hydrochloride (IV) in a 95% yield upon acid hydrolysis. The alcoholic solution of the above hydrochloride, treated with pyridine, gave a quantitative yield of DL-glutamic acid (V).

[1]*Manuscript received June 20, 1956.*
Contribution from the Department of Biochemistry, Faculty of Medicine, Laval University, Quebec City. Paper presented before the Division of Chemistry at the 23rd Meeting of L'Association canadienne-française pour l'avancement des sciences (A.C.F.A.S.), Ottawa, November 5th, 1955.



The β-propiolactone condensation has also been successfully tried with ethyl acetamidocyano-acetate and at different temperatures varying between 0° and 78° C. The composition of the hydrolyzates was qualitatively analyzed by paper chromatography and also, which is much better, by paper electrophoresis. The best conditions found were those already described above for the condensation at 0° C. between β-propiolactone (I) and diethyl acetamidomalonate (II).

It is of interest to note that the diethyl N-acetyl-2-carbethoxyglutamate (III), isolated in the course of the reaction, had a melting point of 66–67°, after several recrystallizations, instead of 81–82.5° as first described by Morrison (16). However, as shown in the experimental part, our sample was submitted to various analyses and proved to have the exact structure.[2]

EXPERIMENTAL[3]

N-Acetyl-2-carbethoxyglutamic Acid Diethyl Ester (III)

In an Erlenmeyer flask fitted with a Y glass adapter and a calcium chloride tube is placed 50 ml. of absolute ethanol. Metallic sodium (1.2 gm., 0.057 mole) is dissolved in it, followed by diethyl acetamidomalonate (II) (10.85 gm., 0.05 mole). The mixture is stirred at room temperature for 30 min. and then cooled to −10° C. in a salt–ice bath. β-Propiolactone (I) (5.0 gm., 0.069 mole) is added in small portions at such a rate that the temperature of the reactants does not rise above 0° C., the addition requiring about 30 min. The mixture is then allowed to stand for 12 hr. during which time the ice is allowed to melt. Anhydrous hydrogen chloride is bubbled in the solution to ensure complete esterification. The mixture is then evaporated to dryness *in vacuo* and the residue extracted with ether. Petroleum ether is added to the concentrated etherous solution which is then placed in the cold. The precipitate recrystallizes either from ether – petroleum ether or an alcohol–ligroin mixture. Yield, 10.8 gm. (68%); m.p. 66–67°. (Lit.: m.p. 81–82.5° (16).) Anal. Calc. for $C_{14}H_{23}O_7N$: N, 4.41. Found: N, 4.44.

[2]*After this manuscript had been submitted for publication, we learned (17) that Dr. G. H. Cocolas has identified the product m.p. 81–82.5° as being in fact 5,5-dicarbethoxy-2-pyrrolidone, which by acid hydrolysis gives glutamic acid.*

[3]*Melting points are uncorrected.*

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Titration of that product with 0.1 *N* sodium hydroxide showed the complete absence of a free acid group whereas its saponification equivalent was near the theoretical value, therefore proving the presence of three ester groups.

The N-acetyl-2-carbethoxyglutamic acid diethyl ester (III) has been found by Morrison (17) to give crystals melting at 82–83° and occasionally at 88–89°. A crude sample, kindly supplied by Dr. Morrison, was recrystallized from ethanol–ligroin to give a first crop of crystals melting at 66–67° with no depression of the m.p. upon admixture with our preparation of m.p. 66–67°. A second crop m.p. 81–82° was also obtained.

When both samples were hydrolyzed and submitted to paper electrophoresis, they gave spots identical with authentic glutamic acid and no trace of glycine, therefore excluding any possibility of contamination by unreacted diethyl acetamidomalonate (II).

Glutamic Acid Hydrochloride (IV)

N-Acetyl-2-carbethoxyglutamic acid diethyl ester (III) (5.0 gm., 0.0158 mole) was heated under reflux for five hours in 100 ml. of dilute hydrochloric acid (1:1). The solution was evaporated to dryness *in vacuo* and the residue recrystallized from alcohol–ether. Yield, 2.75 gm. (95%); m.p. 190°. (Lit.: m.p. 192–193° (9).) Anal. Calc. for $C_5H_9O_4N.HCl$: Cl, 19.3; N, 7.63. Found: Cl, 19.0; N, 7.62.

Glutamic Acid (V)

Glutamic acid hydrochloride (IV) (1.0 gm., 0.005 mole) was dissolved in hot ethanol and one equivalent of pyridine added, causing an immediate separation of the free amino acid. Yield, 0.8 gm. (100%); m.p. 190°. (Lit.: m.p. 198° (23).) Anal. Calc. for $C_5H_9O_4N$: N, 9.52. Found: N, 9.46.

The benzoyl derivative, recrystallized from ether–ligroin, melted at 150°. (Lit.: m.p. 152° (5).) Anal. Calc. for $C_{12}H_{13}O_5N$: N, 5.57. Found: N, 5.55.

Glutamic Acid (V) in a One-step Reaction from β-Propiolactone (I)

The condensation in absolute ethanol at 0° C. between β-propiolactone (I) (5.0 gm., 0.069 mole) and sodium salt of diethyl acetamidomalonate (II) (10.85 gm., 0.05 mole) was carried out as described above for the preparation of N-acetyl-2-carbethoxyglutamic acid diethyl ester (III). When the mixture had reached room temperature, after a 12 hr. stirring, it was poured into water containing one equivalent of hydrochloric acid and evaporated to dryness *in vacuo*. The residue was dried by distilling benzene–ethanol from it, followed by ether extraction and evaporation of the solvent. The oily residue was heated under reflux for five hours in 200 ml. of hydrochloric acid (1:1) and evaporated to dryness *in vacuo*. The residue was dissolved in hot ethanol and pyridine (one equivalent) added. The glutamic acid, which crystallized in the cold, was collected. Yield, 6.4 gm. (87%); m.p. 190°. (Lit.: m.p. 198° (23).) Anal. Calc. for $C_5H_9O_4N$: N, 9.52. Found: N, 9.43.

ACKNOWLEDGMENTS

The authors are indebted to the National Research Council of Canada for Research Fellowships awarded to one of them (G.T.).

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BASIC ESTERS OF SUBSTITUTED PYRIMIDINE-4-CARBOXYLIC ACIDS[1]

By Gordon A. Grant, Carl von Seemann, and Stanley O. Winthrop

ABSTRACT

A number of β-dialkylaminoethyl esters of 2,5-disubstituted pyrimidine-4-carboxylic acids have been synthesized and characterized as their hydrochlorides and in some cases as their methobromide and methiodide salts. Mucochloric acid has been condensed with *S*-methylisothiouronium sulphate to give 2-methylthio-5-chloropyrimidine-4-carboxylic acid, and the corresponding 5-bromo- acid has been converted to the 5-amino- acid.

INTRODUCTION

In the course of some investigations on new antispasmodic and antisecretory agents carried out in this laboratory, our attention was drawn to the possibilities offered by certain 2,5-disubstituted pyrimidine-4-carboxylic acids. 2-Methyl-5-chloro- and 2-methyl-5-bromo-pyrimidine-4-carboxylic acids have been described by Buděšínský (1), and 2-methylthio-5-bromo-pyrimidine-4-carboxylic acid by McOmie and White (2).

The corresponding 2-methylthio-5-chloropyrimidine-4-carboxylic acid was prepared by condensing mucochloric acid with *S*-methylisothiouronium sulphate, using triethylamine as condensing agent. This acid could not be converted to the corresponding 5-amino- acid by heating with concentrated ammonia at 100° for two hours; on the other hand, the corresponding 5-bromo- acid gave a good yield of the 5-amino- acid when subjected to the same procedure.

For the preparation of the basic esters, the above acids were converted to their respective acid chlorides by means of thionyl chloride. No attempt at purification was made and the crude acid chlorides were condensed with two equivalents of the respective basic alcohol in benzene. The basic esters were either isolated as oils or converted directly from their benzene solutions to hydrochlorides or quaternary ammonium salts, listed in Table I. Attempts to prepare basic esters of 2-methylthio-5-aminopyrimidine-4-carboxylic acid were not successful.

Some of the compounds listed in Table I were screened by our Pharmacology Department and were found to be moderately active antispasmodics.

EXPERIMENTAL

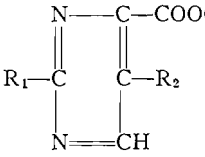
2-Methylthio-5-chloropyrimidine-4-carboxylic Acid

This acid was prepared by the condensation of *S*-methylisothiouronium sulphate with mucochloric acid according to the procedure of McOmie and White (2) for the analogous 5-bromo- compound. One recrystallization from

[1]*Manuscript received March 23, 1956.*
Contribution from Research Laboratories, Ayerst, McKenna & Harrison Limited, Montreal, Quebec.

TABLE I

BASIC ESTERS OF SUBSTITUTED PYRIMIDINE-4-CARBOXYLIC ACIDS



R_1	R_2	R_3	Salt	Recrystal. solv.	M.p., ° C.	Formula	Nitrogen, % Calc.	Found
CH_3S	Br	Isopropyl	HCl	*a*	135–136	$C_{14}H_{23}O_2N_3SClBr$	10.17	10.01, 9.97
CH_3S	Cl	Isopropyl	HCl	*a*	145–147 (decomp.)	$C_{14}H_{23}O_2N_3SCl_2$	11.40	11.21, 11.21
CH_3	Cl	Isopropyl	HCl	*a*	155 (decomp.)	$C_{14}H_{23}O_2N_3Cl_2$	12.50	12.68, 12.37
CH_3	Br	Isopropyl	HCl	*a*	144–145 (decomp.)	$C_{14}H_{23}O_2N_3ClBr$	11.02	10.69, 11.08
CH_3S	Cl	Ethyl	HCl	*b*	183 (decomp.)	$C_{12}H_{19}O_2N_3SCl_2$	12.30	11.90, 12.06
CH_3S	Cl	Ethyl	CH_3Br	*b*	159–160	$C_{13}H_{21}O_2N_3SClBr$	10.52	10.28, 10.28
CH_3S	Cl	Ethyl	CH_3I	*c*	153–154 (decomp.)	$C_{13}H_{21}O_2N_3SClI$	9.44	9.58, 9.40
CH_3S	Cl	Methyl	HCl	*b*	185–186 (decomp.)	$C_{10}H_{15}O_2N_3SCl_2$	13.45	13.56, 13.15
CH_3S	Cl	Methyl	CH_3Br	*b*	203–204 (decomp.)	$C_{11}H_{17}O_2N_3SClBr$	11.33	11.53, 11.67
CH_3S	Cl	Methyl	CH_3I	*b*	198 (decomp.)	$C_{11}H_{17}O_2N_3SClI$	10.05	9.49, 9.76

NOTE: *a—from benzene–acetone; b—from methanol–ether; c—from methanol–acetone–ether.*

aqueous ethanol with decolorizing carbon gave yellow platelets, m.p. 169–170° C. Calculated for $C_6H_5N_2ClSO_2$: C, 35.22; H, 2.46; Cl, 17.33%. Found: C, 35.36, 35.83; H, 2.32, 2.71; Cl, 16.87, 17.12%.

2-Methylthio-5-aminopyrimidine-4-carboxylic Acid

2-Methylthio-5-bromopyrimidine-4-carboxylic acid was treated with concentrated ammonium hydroxide according to the procedure described by Buděšínský (1), for the preparation of the analogous 2-methyl-5-amino compound. The product, 2-methylthio-5-aminopyrimidine-4-carboxylic acid, on recrystallization from water, gave long yellow needles, m.p. 190–191.5° C. (decomp.). Calculated for $C_6H_7N_3O_2S$: C, 38.91; H, 3.81; N, 22.69%. Found: C, 39.37; H, 4.04; N, 22.35%.

β-Diethylaminoethyl-2-methylthio-5-chloropyrimidine-4-carboxylate

Five grams of 2-methylthio-5-chloropyrimidine-4-carboxylic acid was refluxed with 12 ml. thionyl chloride until completely dissolved (four and one-half hours). Excess thionyl chloride was removed under reduced pressure, five successive 10 ml. portions of anhydrous benzene being added to the residue. The resulting oil was considered to be sufficiently pure 2-methylthio-5-chloropyrimidine-4-carboxylic acid chloride to be used as such in the subsequent esterification.

The acid chloride was dissolved in 25 ml. anhydrous benzene, and freshly distilled β-diethylaminoethanol (5.73 gm., 2 moles per mole of acid), dissolved in 25 ml. benzene, was added slowly with stirring under anhydrous conditions. The initially vigorous reaction was completed by refluxing for five hours and the mixture was then allowed to cool to room temperature overnight.

β-Diethylaminoethanol hydrochloride (3.70 gm., 98.5% of theory) was separated as a by-product by filtration, and the benzene filtrates were washed with eight 50 ml. portions of water to pH 8.1 and dried with anhydrous

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sodium sulphate. Evaporation of the solvent yielded 6.3 gm. (85% of theory) β-diethylaminoethyl-2-methylthio-5-chloropyrimidine-4-carboxylate, a brown oil which could not be brought to crystallization (the corresponding β-dimethylaminoethyl ester crystallized spontaneously, m.p. 120–121° C.).

The above basic ester (3.15 gm.) was dissolved in 25 ml. anhydrous ether and an equimolecular amount (0.38 gm.) of dry hydrogen chloride in ether solution was added. The resulting gummy precipitate was repeatedly washed with ether, dried *in vacuo*, dissolved in 20 ml. hot methanol, treated with a little decolorizing carbon, filtered, and crystallized by addition of 75 ml. ether to the filtrate, giving the crude hydrochloride, m.p. 176–177° C. (decomp.), recrystallized from methanol–ether to yield 91% of theory of the pure compound, m.p. 183° C. (decomp.).

Further samples of the basic ester were treated in ether solution with large excesses of methyl bromide or methyl iodide, keeping the mixture at 60° for four days followed by several days at room temperature. The precipitates were purified as above by dissolving in methanol, treating with decolorizing carbon, and crystallizing by addition of ether. The methobromide was thus obtained with m.p. 159–160° C. and the methiodide with m.p. 153–154° C.

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LIGHT ABSORPTION STUDIES

PART V. THE RELATION OF MESOMERIC EFFECTS AND ULTRAVIOLET LIGHT ABSORPTION SPECTRA[1]

By W. F. Forbes and Audrey S. Ralph

ABSTRACT

A method for the determination of *mesomeric* effects from ultraviolet light absorption data is critically discussed. For halogen-substituted compounds, the method gives an order of *mesomeric* effects different from that which is usually accepted for the halogens.

INTRODUCTION

It was noted in Part II (16) of this series that the spectra of *para*-substituted benzoic acids may be related to the *mesomeric* but not to the *inductive* effect of the substituent group. It was shown in particular that both wavelength displacements towards longer wavelengths and intensities of absorption (ϵ) for the halogen-substituted compounds were in the order $-I > -Br > -Cl > -F$.

Electronic spectra, like other physical properties, would be expected to require consideration primarily of the ground states of molecules; these will determine the excited states, and the main difference between the ground and excited states will be that the proportion of contributing forms will vary. Thus the electron-displacement effects which we chiefly have to take into account will be the *inductive* and the *mesomeric* (or resonance) effect. We use these terms to indicate the different types of electron displacements and the terms do not necessarily correspond to the usage with which they have been associated in other fields of study (cf. discussion section). We propose to designate as *inductive* effects, electronic interactions which are proportional to the electronegativites of the atoms concerned, and which decrease with the distance between the two interacting centers. By the *mesomeric* effect (or resonance effect) we shall designate electronic interactions which give rise to what has been termed resonance forms. The latter, therefore, would be equal, for example, for *ortho*- and *para*-methylacetophenones, since the contributing resonance structures are generally assumed to be similar. Both *inductive* and *mesomeric* effects will consequently affect both ground and electronic excited states, and it is the purpose of this paper to present a self-consistent picture of the changes observed in halogen-substituted benzenes.

Normally, a shift to longer wavelength accompanied by increased intensity of absorption represents a "closing-up" of electronic levels of the ground and excited states and thus a decrease in transition energy. Since the excited states have been shown (cf. 21) to be mainly dipolar, these dipolar forms will contribute more to the excited than to the ground states. This "closing-up" of the energy levels therefore represents a more ready formation of excited states. Hence, the data show that the dipolar states are attained more easily in the

[1]*Manuscript received April 27, 1956.*
Contribution of the Memorial University of Newfoundland, St. John's, Newfoundland.

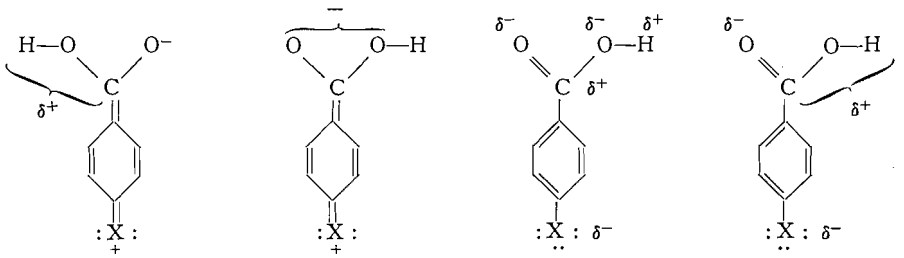
order $-I > -Br > -Cl > -F$, that is the potential energy of the excited states is lowered in the order $-I > -Br > -Cl > -F$. Since it is conclusively established that *inductive* effects are in the order $-F > -Cl > -Br > -I$ (20, 23, and references cited therein), which would indicate the reverse order of the observed effects, one is led to the conclusion that the *mesomeric* effect may account for the observed data. This supposes the *mesomeric* effect to be in the order $-I > -Br > -Cl > -F$, again the reverse of the accepted order (20), but the evidence for the *mesomeric* effects being in the order $-F > -Cl > -Br > -I$ appears to be far less conclusive than the evidence for the *inductive* effects.

Further, *inductive* effects, which are generally supposed to decrease rapidly as the distance between the two chromophores increases, would not be the same in the *ortho*- and *para*-positions. Yet spectral data indicate (13) that in the absence of steric effects, spectra obtained from *ortho*- and *para*-substituted compounds are similar.

This then points to conjugation, or resonance, effects and in particular to the *mesomeric* effect as the explanation of the observed changes. The present communication examines some of the implications in assuming the spectral changes to be due to the *mesomeric* effect, this being in the order of $-I > -Br > -Cl > -F$.

ULTRAVIOLET ABSORPTION SPECTRA

The B-band of halogen-substituted benzoic acids in the ultraviolet region may be correlated with transitions involving mainly dipolar excited states. These may be crudely represented by structures of type I (illustrating *mesomeric* effects) and by structures of secondary importance (type II; illustrating *inductive* effects, that is involving electrostatic influences of the valency electrons of the halogen atom only).



I*A* I*B* II*A* II*B*

The values for the *mesomeric* effects which may be thus obtained for halogens and other atoms or groups can then be directly compared with the accepted values, as established by the evidence of dipole moments and chemical equilibria.

By using *para*-disubstituted compounds, not only are *inductive* effects minimized but steric effects may be neglected as a first approximation. There is some evidence for second-order effects under the latter heading (15), since

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minor steric effects probably operate even in *para*-disubstituted compounds, because of the adjoining hydrogen atoms. Under the heading of *inductive* effects also, a large number of second-order effects suggest themselves, for example, *inductive* effects of the halogen atom directly on the carboxyl-group or intermolecular *inductive* effects. However, it has already been shown that *inductive* effects generally must be small; this was deduced from the similarity of *ortho*- and *para*-disubstituted benzene derivatives, in the absence of steric effects (cf. Table I of Part III (13)). This therefore leads to the conclusion that most of these second-order *inductive* effects similarly play only a minor part in determining transition energies.

Another argument against the predominance of *inductive* effects, even in the spectra of *meta*-disubstituted compounds, is provided by the relevant data of benzoic acids and acetanilides (16). It is found that in the *meta*-substituted compound, where the *mesomeric* effect by definition is small, the spectrum generally resembles that of the parent compound. Consequently, if the *inductive* effect is of little importance in determining the transition energies of *meta*-compounds, it seems reasonable to suppose it to be even less for the corresponding *para*-isomers.

A further reason why induced polarization may be regarded as small is that in fluoro-substituted compounds, where the *inductive* effect should be greatest, hardly any change is observed by comparison with the parent compound (see Table II). This argument is strengthened by the fact that any steric effect of the fluorine atom is small and thus second-order steric factors cannot readily be postulated to oppose any *inductive* effects.

It is of interest to note at this stage that similar relationships, namely resemblances between *ortho*- and *para*-disubstituted benzene derivatives, are not observed for dissociation constants. Thus while it may now be taken as established that the B-band of *para*-halogen substituted compounds is determined predominantly by the *mesomeric* effect, a similar relationship does not follow for the other physical properties under consideration.

The relevant spectra in absolute ethanol are collected in Table I. The $\Delta\lambda$ values, where $\Delta\lambda = \lambda_2 - \lambda_1$, and λ_2 and λ_1 represent the locations of maximal absorption of the main absorption bands of *para*-halogen substituted and parent compounds respectively, are shown in Table II.

TABLE I

MAXIMA (mμ) OF B-BANDS OF COMPOUNDS *p*-R.C_6H_5X

	X =									
	H		F		Cl		Br		I	
R	λ	ε	λ	ε	λ	ε	λ	ε	λ	ε
—COOH (16)	227	11,000	228	11,000	234	15,000	238.5	16,000	252	17,000
—H (4, 11)	203.5	7,400	204	6,200	210	7,500	210	8,600	226	13,000
—$NHCOCH_3$ (16)	242	14,500	240	13,000	249	18,000	252	18,500	254	23,000
—$N(Me)_2$ (24)	250	13,600	247	12,300	259	17,000	260	19,600	—	—
—$COCH_3$ (15)	240	12,500	242	11,500	249	16,000	253	16,000	262	16,000
—CHO (15)	244	13,000	245	12,000	254	15,000	257	16,000	—	—

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TABLE II

Δλ VALUES IN Mμ FOR *para*-HALOGEN SUBSTITUTED COMPOUNDS DESCRIBED IN TABLE I

	X =			
R	F	Cl	Br	I
—COOH	1	7	11.5	25
—H	0.5	6.5	6.5	22.5
—$NHCOCH_3$	−2	7	10	12
—$N(Me)_2$	−3	9	10	—
—$COCH_3$	2	9	13	22
—CHO	1	10	13	—

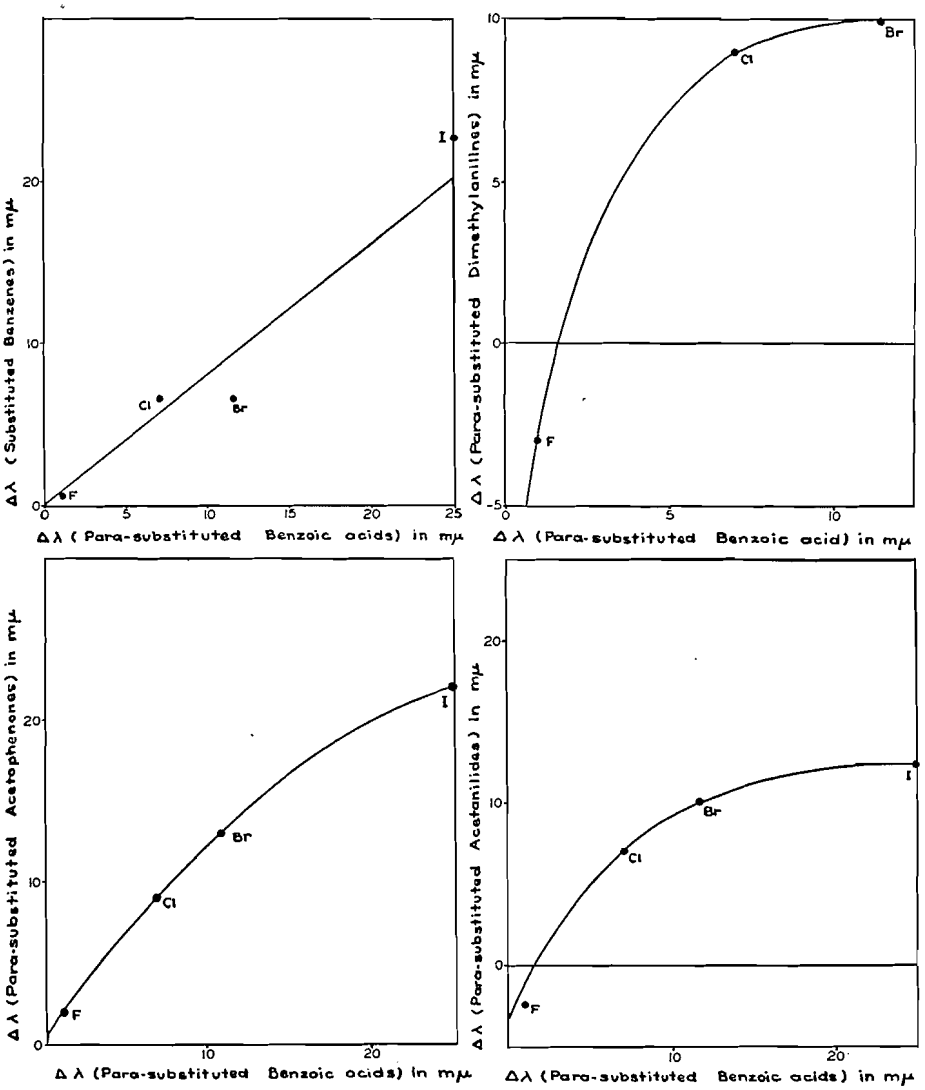

FIG. 1.

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The $\Delta\lambda$ values for substituted benzenes, *para*-substituted acetophenones, *para*-substituted acetanilides, and *para*-substituted N,N-dimethylanilines are also compared with the $\Delta\lambda$ values obtained for the corresponding benzoic acids in Fig. 1.

Fig. 1 and Table II show that *mesomeric* effects are of approximately the same significance in halogen-substituted benzenes and in *para*-halogen substituted benzoic acids, acetophenones, and benzaldehydes. The slopes of the approximately straight lines thus obtained are about 45°, indicating equal displacements for the above-mentioned compounds due to *mesomeric* effects. The corresponding acetanilides and N,N-dimethylanilines, compared with benzoic acids, generally suggest slopes initially greater than 45°, but flattening out considerably towards the larger iodine atom (see Fig. 1).

A tentative interpretation of these observations may now be made. The *mesomeric* effect is caused in benzoic acids, benzaldehydes, and acetophenones primarily by the halogen atom; in the presence of a nitrogen atom, because of its unshared electrons additional conjugation enhances the congestion of electrons in the *para*-positions and this causes:

(I) A greater *mesomeric* interaction, since the effect is now able to operate more extensively (cf. also the different *mesomeric* moments obtained from dipole moment data (2)).

(II) An increase of second-order steric effects, due to interaction of the halogen atom with the now increased electron density. This becomes appreciable with the bulky iodine atom and may explain the anomalously low value for *p*-iodo-N,N-dimethylaniline.

It may be noted that in Table II and Fig. 1, wavelength changes rather than changes in the observed intensities have been chosen as the measure of electrical effects. Although both give the correct order, since the increased *mesomeric* effect also gives rise to increased transition probability, wavelength changes are more conveniently converted into energy values. Further there is evidence (cf. 12, 13, 14) that values of transition probabilities as measured by the absorption intensity (ϵ) are more susceptible to small steric effects, and other second-order interactions.

Another recent interesting example has been provided by the spectra of α'-halogen-substituted 4-methoxy-4′-methyldiphenyls (see Table III).

TABLE III

MAXIMA ($m\mu$) OF B-BANDS OF COMPOUNDS *p*-MeO.C_6H_4.C_6H_4.CH_2X ACCORDING TO BURAWOY AND SPINNER (8), AND $\Delta\lambda$ VALUES FOR THESE AND *para*-SUBSTITUTED BENZOIC ACIDS

X	λ	ϵ	$\Delta\lambda$	$\Delta\lambda$ (Benzoic acids)
H	260	23,600	0	0
Cl	271	23,000	11	7
Br	277	23,500	17	11.5
I	291	23,500	31	25

Although Burawoy and Spinner (8) explain the spectral changes by the "polarizability" of substituents, the spectra of these diphenyls also fit in well with our assumption. The $\Delta\lambda$ changes of the diphenyls are proportional to other $\Delta\lambda$ changes already described and hence to the proposed *mesomeric* effects. This example also emphasizes the advantages of considering wavelength changes rather than absorption intensities, since here the intensities are fairly close together.

The example finally reinforces the assumed steric hindrance of the iodine atom since the iodine atom in α'-iodo-4-methoxy-4'-methyldiphenyl is separated by a methylene group from the phenyl group, consequently causing considerably less steric interaction. In accordance with our hypothesis, the steric effect associated with high electron densities around the halogen atom is no longer observed, and the $\Delta\lambda$ value for the iodo-compound concurs with the expected value.

DISCUSSION

Both dipole moment and acid dissociation data have been extensively used to obtain values for the *mesomeric* effect of the halogen atoms (1, 2, 3, 17, 18, 19, 20, 26, 27). From both these methods it is difficult to obtain consistent results for the *mesomeric* effect and this may be ascribed primarily to the difficulty of obtaining a suitable reference compound (both dipole moment data and dissociation constant data are determined by ground states which unlike electronic spectra cannot be adequately described in terms of *mesomeric* and steric effects alone). Secondly, solvent effects play a large part in both methods, and this type of interaction does not appear to have been fully elucidated. These difficulties become appreciable on closer examination (such an examination has been carried out, but has been excluded from this paper for the sake of brevity), and it may be concluded that dipole moment data and acid dissociation data provide a less satisfactory method than ultraviolet absorption data for determining values of *mesomeric* effects.

An indication in favor of our argument may, however, be obtained from the graphs (see Fig. 2), which show reasonable agreement between the changes due to *mesomeric* effects obtained from acidity constant data (cf. 20) and those from light absorption data.

On plotting $\Delta\lambda$ values against values of the acidity constants, similar curves are obtained, namely, initially almost straight lines with a distinct "bending" or "flattening-out" towards the iodine value. This "flattening-out" has been ascribed previously to second-order steric factors and an analogous interpretation is proposed for the effect in this instance. This would suggest that acidity constants are more susceptible to steric effects than are light absorption spectra, an observation which will be referred to again (see below).

Also noteworthy is the consideration that reaction rate constants are less likely to yield accurate values of *mesomeric* effects, since the interaction of two or more molecules will introduce additional variables. For example, since the orienting influence of a group in chemical substitution may depend on polarizability factors called into operation upon the approach of a reactive

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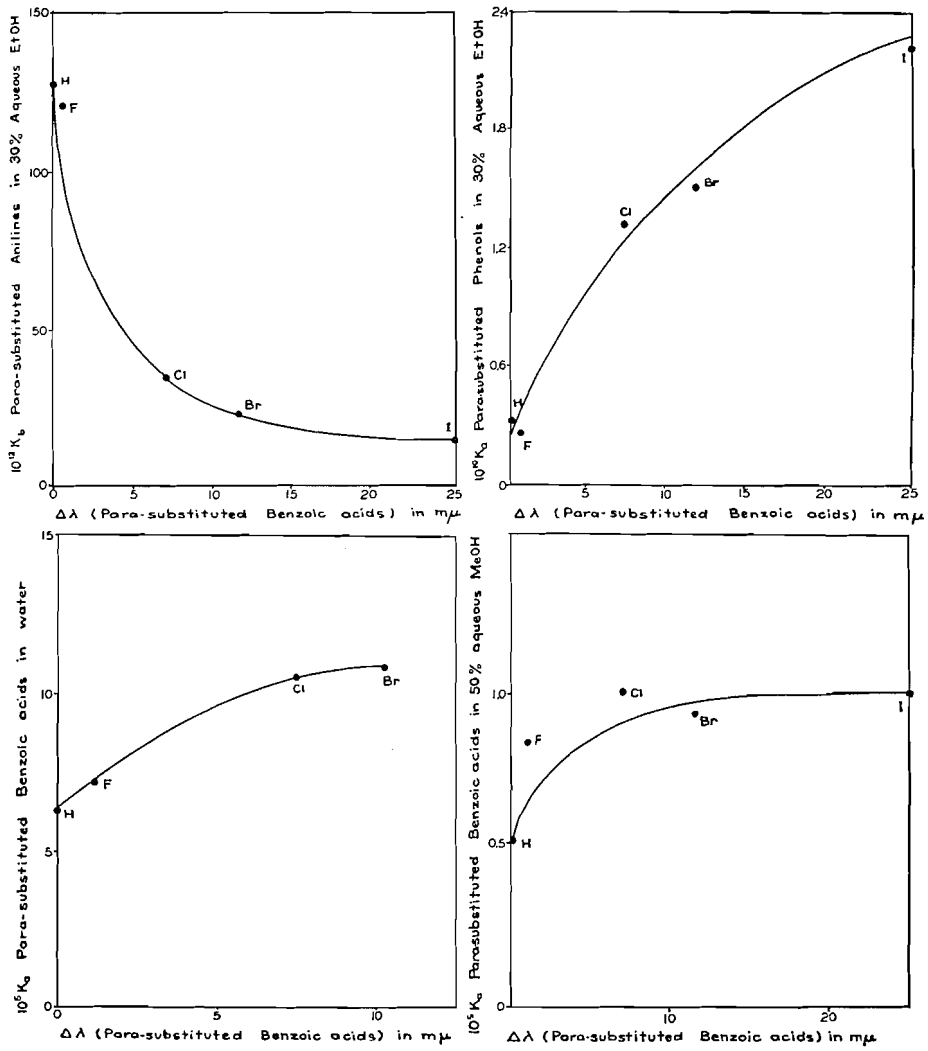

FIG. 2.

center, there is no assurance that the result is a measure of the electronic situation in the "resting molecule", as normally measured in dilute solution spectra. Nevertheless, the following conclusions seem to emerge from the data presented so far:

1. Information indicating the existence and relative magnitude of *mesomeric* effects can be obtained from reaction rates, dipole moment data, equilibrium constants, light absorption data, and other physical constants. Whether the *mesomeric* effect involves a disturbance of electrons from one atom to another, as has been proposed in the classical conception of mesomerism, or merely an *inductive* electron displacement, as has been suggested by Burawoy and others (cf. 7, 8, 22, 25), perhaps cannot be decided conclusively. If, however,

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the latter hypothesis is so formulated as to suggest a decreased interaction as the distance between the chromophores increases—and so predict a dissimilarity in *ortho-* and *para*-substituted compounds—it must be deemed the less satisfactory explanation of the observed phenomena. Some recent theoretical examinations on spectral properties of alkyl-substituted compounds also suggest that energy shifts resulting from *inductive* effects *alone* will be positive, thus leading to hypsochromic shifts (9, 10). Therefore it may be concluded that normally whenever an over-all bathochromic shift occurs, the bathochromic shift due to the *mesomeric* effect must be of larger magnitude than any *inductive* effect.

2. It seems an unjustified assumption to associate the *mesomeric* effect in different compounds with one and the same dipolar excited state. For example, while one particular dipolar excited state, such as I*A*, may well be associated with the *mesomeric* effect in certain compounds, other dipolar structures, such as I*B*, may become more important on introducing other substituents. This lack of uniformity is illustrated by a recently described effect in the spectra of substituted benzaldehydes and acetophenones. There, the *para*-methyl group reduces steric interaction in 2,4,6-trimethylbenzaldehyde and 2,4-dimethylacetophenone, but increases it in 2,4,6-trimethylacetophenone (5). This phenomenon was ascribed to additional conjugation, *either* overcoming *or* further enhancing steric interactions already present. This explanation may incidentally be used to relate two other phenomena previously referred to in this paper. First, it was noted that slight steric interactions, of the type postulated in chemical equilibria, do not show up as well in light absorption properties (see Fig. 2). This may be because light absorption properties involve, to a larger extent, excited states in which the slight steric hindrance is more readily overcome (see also Fig. 3). Secondly, it was observed that a fluorine-substituted compound, with respect to the parent compound, may cause a slight negative wavelength shift (see Table II). This negative shift may now be tentatively explained by saying that the halogen atom cannot always immediately exert its *mesomeric* effect, if the latter is small. This tendency would again be more pronounced in excited states and may result in, at first, a positive energy displacement (hypsochromic shift), until the positive *mesomeric* effect becomes sufficiently large to lower again the potential energy of the excited state (or in other words, until the more usual electronic excited state again predominates).

3. The relative importance of *mesomeric* effects appears to be quite different, in properties like dipole moment and acidity constant data on the one hand, and in light absorption properties on the other. The chief difference between the two sets of properties, from our point of view, appears to be that only light absorption data involve transitions to excited states, which are largely dipolar in character. Because of the nature of these excited states, one would expect them to be more susceptible to *mesomeric* effects. Consequently, the apparent preponderance of *mesomeric* effects in light absorption data of the halogens—as evidenced from the observed wavelength changes in conjunction with the proposed order of *mesomeric* effects, and from the identity of some *ortho-* and *para*-isomers—is perhaps not surprising.

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It may therefore be postulated that *mesomeric* interaction in ultraviolet light absorption is only of secondary importance in ground states and that the potential energy levels of ground states for the *para*-halogen substituted compounds are roughly equal (cf. dipole moment data and dissociation constants). In excited states *mesomeric* effects will predominate, and it is suggested that the representation of the transitions involved is approximately as shown in Fig. 3.

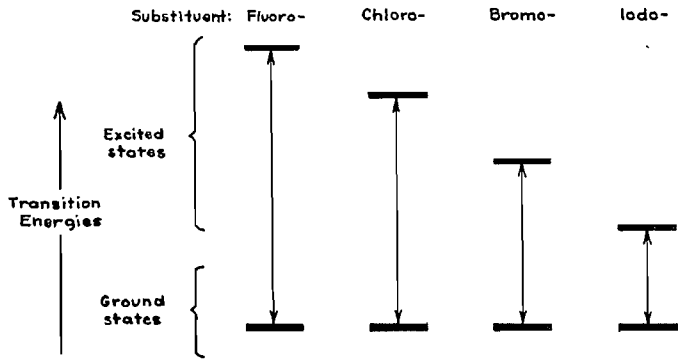

FIG. 3. Schematic representation of transitions in *para*-halogen benzoic acids after Braude and Waight (6).

Fig. 3 illustrates why the *mesomeric* effect is readily identified in light absorption data, and why it is much less easily identified from dipole moment data and acid dissociation data.

4. Although it is questionable how a knowledge acquired about *mesomeric* effects in the excited state is applicable to ground states and vice versa, a simple semiquantitative interpretation of *mesomeric* effects in the excited state is attempted. Thus it may be hoped that when the percentage of dipolar forms in the excited and ground states have been calculated, it will be possible to obtain measures of the *mesomeric* effects in various ground states.

In the meantime, the wavelength changes for halogen-substituted benzenes and *para*-halogen substituted benzoic acids have been used to evaluate the approximate energy gains associated with *mesomeric* effects in these compounds. These values are recorded in Table IV. It may be noted that on the

TABLE IV

APPROXIMATE POTENTIAL ENERGY GAINS (IN KCAL./MOLE) IN THE PHOTO-EXCITED STATE OF HALOGEN-SUBSTITUTED BENZENES AND BENZOIC ACIDS DUE TO MESOMERIC EFFECTS

Substituent	Wavelength changes in mμ (see Table II)		Approx. energy gain (in kcal./mole)
	Benzenes	Benzoic acids	
—F	1	0.5	0.5
—Cl	7	6.5	4
—Br	11.5	6.5	5
—I	25	22.5	13

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basis of very simplified calculations the change in dipole moments from fluoro- to iodo-benzenes due to *mesomeric* effects, according to the values reported by Groves and Sugden (18, the latest available gas-phase values), amounts to an energy change of only approximately 3 kcal./mole. This, as expected, is much less than the value obtained from Table IV (approximately 13 kcal./mole), and confirms the hypothesis that *mesomeric* interactions in ultraviolet absorption spectra mainly affect the electronic excited states.

EXPERIMENTAL

Except for minor deviations in procedure, the compounds, the spectral properties of which were not previously known, were prepared by standard methods as described in the literature. Purification was effected by distillation under vacuum and was deemed adequate when redistillation resulted in no further measurable change in the absorption spectrum.

The spectra were determined on a Unicam SP 500 spectrophotometer using standard methods.

ACKNOWLEDGMENTS

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THE REACTIONS OF ACTIVE NITROGEN WITH METHANE AND ETHANE[1]

By P. A. Gartaganis and C. A. Winkler

ABSTRACT

Reinvestigation of the active nitrogen – methane reaction in the temperature range 45° to 500°C. has confirmed hydrogen cyanide as the only product, other than hydrogen, formed in measurable amounts. An "induction" effect in the hydrogen cyanide production was observed with increase of methane flow rate. This induction decreased with increase of temperature and was shown to be due to concomitant hydrogen atom reactions, since it could be eliminated by addition of hydrogen atoms to the reaction mixture. Reinvestigation of the active nitrogen – ethane reaction over the temperature range −100° to 475°C. also confirmed hydrogen cyanide to be the only measurable product, other than hydrogen, of that reaction. There was some indication that an induction effect was present with ethane, as with methane, and it may be concluded tentatively that both reactions are carried substantially by hydrogen atom reactions.

INTRODUCTION

In a previous study in this laboratory (7), it was observed that the Arrhenius plot for the reaction of active nitrogen with neopentane showed a marked change of slope, indicative of two activation energies in the range of temperatures used. While there was some reason to believe that this behavior might be due to two reactive species in active nitrogen, one of which is almost certainly atomic nitrogen (4, 5), there remained the possibilities that it resulted from concomitant hydrogen atom reactions or from different rates of attack by a single species in active nitrogen at the primary and quaternary carbon atoms in the neopentane molecule. Since methane and ethane are incapable of suffering such different modes of attack, the reactions of active nitrogen with these two hydrocarbons have been reinvestigated over a wider range of conditions than those used previously (3), in an effort to examine further the possible significance of the two activation energies observed with neopentane.

EXPERIMENTAL

The investigations were made with conventional fast-flow techniques. In many experiments with methane, hydrogen atoms were introduced simultaneously with nitrogen atoms. The arrangement for doing this is illustrated in Fig. 1, which, with the accompanying legend, serves also to indicate all the essential details of the apparatus currently used in this laboratory for studies on active nitrogen reactions. When necessary, the reaction vessel was surrounded by an electrically heated furnace molded from asbestos or by a plastic vessel to contain an appropriate refrigerant.

The nitrogen discharge tube was operated by a 110 v.–5000 v. transformer which fed through a diode rectifier (Raytheon, 866-A-GAA) and a 2000 ohm resistance into two condensers in parallel (each 4 μf., 6000 v., Aerovox No. 3).

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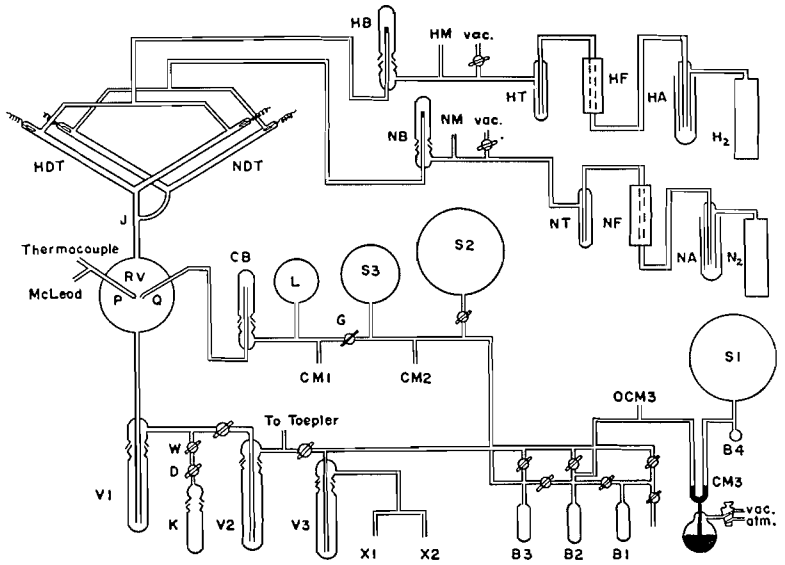

Fig. 1. Diagram of apparatus.
HA, NA: Manostats to control hydrogen and nitrogen inlet pressures. HF, NF: Furnaces filled with copper turnings at 450°C. to remove oxygen from the hydrogen and nitrogen streams. HT, NT: Liquid nitrogen traps to remove water and CO_2 from the hydrogen and nitrogen. HM, NM: Manometers to measure stream pressures. HB, NB: Calibrated capillary flow meters for hydrogen and nitrogen. HDT, NDT: Hydrogen and nitrogen discharge tubes with aluminum electrodes. J: Connecting tube, 20 cm. long, 1.8 cm. diam. RV: Reaction vessel (300 cc.), "poisoned" with phosphoric acid. P: Thermocouple. B1, B2, B3: Bulbs for condensed hydrocarbon. S1: Hydrocarbon storage vessel (5 liters). S2, S3: Calibrated hydrocarbon storage vessels (1100 cc. and 400 cc. respectively). CM1, CM2, CM3: Manometers to measure pressures in hydrocarbon storage vessels. G: Scratched stopcock to maintain constant pressure of hydrocarbon in ballast volume, L. CB: Calibrated flow meter for hydrocarbon. Q: Hydrocarbon jet. V1, V2, V3: Liquid nitrogen product traps. K: Absorber (to contain appropriate solution). X1, X2: Two Cenco "Megavac" pumps (or a single "Hypervac" pump).

These discharged across the discharge tube four to six times per second, depending on the operating pressure. The hydrogen discharge tube circuit was similar, but a variable transformer was inserted in the 110 v. line to permit controlled variation of the discharge frequency in the hydrogen discharge tube.

Hydrogen cyanide was estimated quantitatively by condensing it over frozen potassium hydroxide in the absorber, K, followed by titration of the cyanide with standard silver nitrate after the contents of the absorber had been allowed to come to room temperature.

RESULTS

Methane

Only about 1% of the methane reacted at 45°C., (comparable with the possible amount of impurities present), but significant reaction occurred above 280°C. At 358°C. and 450°C., the reaction showed a striking feature hitherto unobserved in active nitrogen reactions. The yield of hydrogen cyanide was low at low flow rates of methane, but increased rather rapidly as the

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methane flow was increased. At sufficiently high flow rates, the HCN yield became constant at a given temperature, presumably after all the available active nitrogen was consumed. Typical of the results that were obtained in numerous experiments are those shown in Fig. 2. For convenience, the acceleration in hydrogen cyanide production with increased methane flow rate will be designated as an "induction", but it should be realized that it is not an induction period in the usual sense since it is not a function of time but of concentration.

Hydrogen cyanide was the only product of the reaction obtained in measurable quantities over the range of temperatures used. No cyanogen, ammonia, or hydrazine could be detected by usual analytical methods, and the mass spectrometer failed to show more than possible traces of substances that might have been C_2 and C_3 hydrocarbons or cyanogen.

It was suspected that the induction in the reaction might be caused by fast reaction of active nitrogen with methyl radicals derived from attack of methane by atomic hydrogen produced in the initial reaction with active nitrogen. The reaction of methane with active nitrogen in the presence of added molecular and atomic hydrogen was therefore studied in some detail. A large number of experiments were made, the results of which may be summarized briefly to illustrate the behavior observed.

In preliminary experiments in which molecular hydrogen was added to the active nitrogen stream before it entered the reaction vessel, pronounced induction remained. This was also true at temperatures up to 330°C. when a relatively low concentration of atomic hydrogen was added, (low voltage across HDT, Fig. 1), although at higher temperatures (513°C.) this low H atom concentration did cause almost complete disappearance of the induction.

Complete elimination of the induction was achieved with a higher concentration of H-atoms, the total pressure of hydrogen being greater than that of nitrogen. However, the maximal hydrogen cyanide yield was now quite low. Experiments were then made to determine whether the absence of the induction could be maintained without sacrificing the hydrogen cyanide yield. This was finally accomplished by suitable adjustment of the relative concentrations of atomic hydrogen and active nitrogen admitted to the reaction vessel. A final series of experiments was then made at 480°C., with all conditions rigorously controlled, to confirm that the behavior indicated by the many previous experiments could be associated with the operating conditions used, and especially that elimination of the induction was possible for different levels of hydrogen cyanide yield. The primary of the hydrogen discharge circuit was set first at 50 v., then at 100 v., and the hydrogen cyanide yields determined at different methane flow rates in the presence of molecular and atomic hydrogen with the nitrogen pressure greater than and less than that of hydrogen. The results are shown in Fig. 3.

When molecular hydrogen was present at a pressure *lower* than the pressure of nitrogen, some induction could be observed, but when atomic hydrogen was introduced under otherwise similar conditions the induction was eliminated for a relatively high yield of hydrogen cyanide. When the pressure of hydrogen was *greater* than that of nitrogen, no induction was observed under any of the

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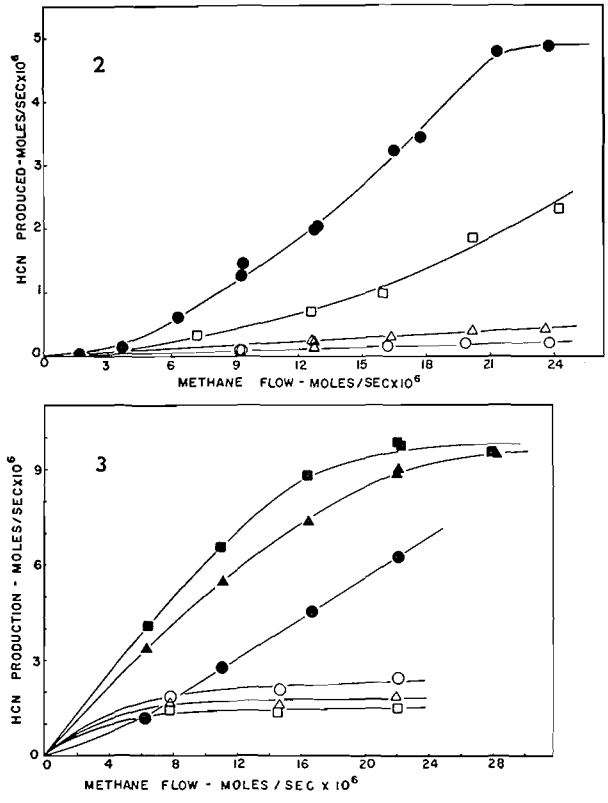

FIG. 2. Relation between hydrogen cyanide production and methane flow rate. Temperature, °C.: ○ 45±3, △ 280±2, □ 358±5, ● 441±6.

FIG. 3. Hydrogen cyanide production as a function of (*a*) methane flow rate, (*b*) voltage in the primary circuit of the hydrogen discharge tube, and (*c*) relative pressures of nitrogen and hydrogen in the reactions methane – active nitrogen, and methane – active nitrogen – hydrogen (molecular or atomic).

Temperature, 480°C.

Pressure:	N_2 high, H_2 low	N_2 low, H_2 high
Voltage in primary of hydrogen discharge circuit:	● No discharge	○ No discharge
	▲ 50 v.	△ 50 v.
	■ 100 v.	□ 100 v.

operating conditions, and the yield of hydrogen cyanide was quite low. Elimination of the induction in the presence of molecular hydrogen, i.e. without the hydrogen discharge in operation, was immediately traced to back diffusion of hydrogen into the nitrogen discharge tube under the pressure differential that prevailed. The characteristic reddish color of the hydrogen discharge was observed near the base of the nitrogen discharge tube, and undoubtedly enough hydrogen atoms were produced to eliminate the induction. It might be noted that the order of the curves in Fig. 3 was reversed when the relative pressures of nitrogen and hydrogen were reversed. Also, substitution of helium for hydrogen, under comparable conditions, had no effect on the induction, i.e. there was no effect of merely increasing the total pressure in the system.

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Ethane

Regardless of ethane flow rate or temperature, hydrogen cyanide was the only gaseous product obtained in measurable amounts from this reaction. No cyanogen, ammonia, or hydrazine was detected chemically or mass spectrometrically. At temperatures below room temperature, small amounts of a dark brown polymer were deposited in the reaction vessel and the main trap.

The relation between hydrogen cyanide production and ethane flow rate over the temperature range −100°C. to 475°C. is shown in Fig. 4. For the data recorded in Fig. 4*A*, no attention was given to the temperature of the

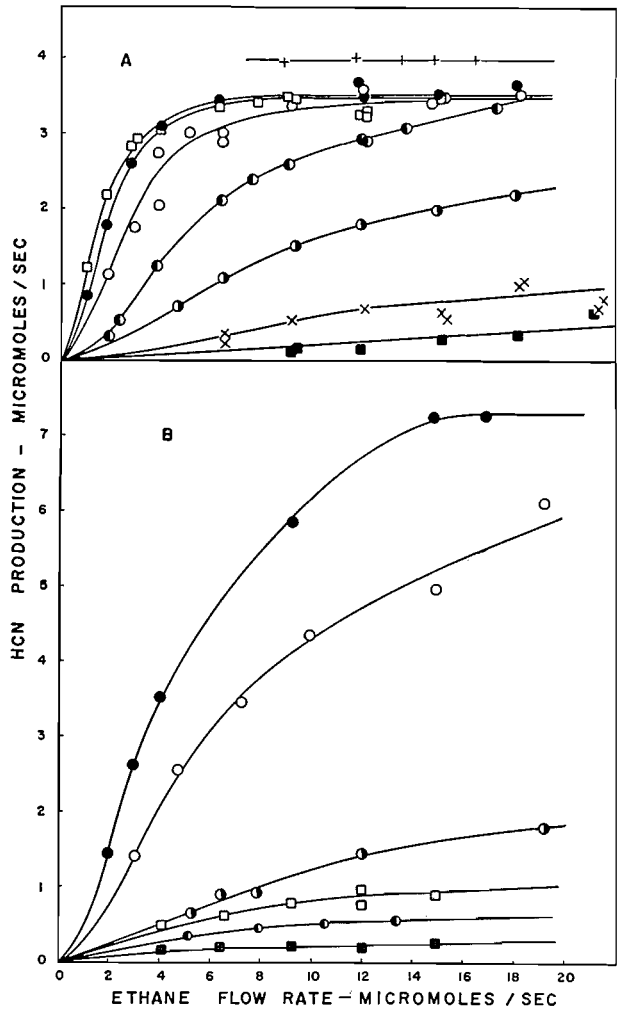

FIG. 4. Relation between hydrogen cyanide production and ethane flow rate.
Temperature, °C.:
A: ■ −100, × −50, ◑ 55, ◐ 175, ○ 298, ● 400, □ 475, (+ Ethylene at 300°C
B: ■ −50, ◐ 3, □ 50, ◑ 122, ○ 253, ● 404.

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tube that connected the reaction vessel to the discharge tube. For the data of Fig. 4*B*, however, the lower half of this connecting tube was surrounded by appropriate refrigerant for the low temperature experiments; also, for these experiments, a new discharge tube and reaction vessel were used, and the active nitrogen concentration, estimated by reaction with ethylene (2, 6, 8), was about twice that in the experiments which yielded the data of Fig. 4*A*.

DISCUSSION

Methane

In the earlier investigation of the reaction of methane with active nitrogen (3), it was concluded that the production of hydrogen atoms in the initial attack on the methane molecule probably had little influence on the yield of hydrogen cyanide. However, the earlier experiments were made for the most part in the neighborhood of 400°C., and with a limited range of methane flow rates. The results of the present study leave little doubt that the reaction is, in fact, carried to a considerable extent by hydrogen atoms, probably by the following sequence of reactions:

$$N + CH_4 \rightarrow HCN + H_2 + H, \quad [1]$$

$$H + CH_4 \rightarrow CH_3 + H_2, \quad [2]$$

$$CH_3 + N \rightarrow HCN + 2H \quad [3]$$

There is little doubt that reaction [3] occurs with a low activation energy (1) and is very fast. Hence, as the methane flow rate is increased and reaction [2] increases in significance relative to recombination of hydrogen atoms, the hydrogen cyanide yield might be expected to show the induction effect observed. Addition of hydrogen atoms should, of course, eliminate the induction by accentuating the contribution of reaction [3] at all flow rates.

The reversal in the order of the curves in Fig. 3, and the drastic change in hydrogen cyanide yield that may be caused by addition of hydrogen atoms, suggest that hydrogen atoms may deactivate active nitrogen, possibly by

$$N + H \rightarrow NH,$$
$$2NH \rightarrow N_2 + H_2.$$

Owing to the induction effect, no reliable estimate of the activation energy of the methane – active nitrogen reaction was possible, but calculations (3) confined to low flow rates of methane, where secondary reactions are presumably minimal, gave an activation energy of about 13 kcal. and a steric factor of about 10^{-2} (cf. $E = 11$ kcal., $P = 5 \times 10^{-3}$ from Ref. 3). In these calculations, the concentration of active nitrogen was assumed to be given by the maximum yield of hydrogen cyanide obtained in the reaction with ethylene (2, 6, 8). In view of its complicating features, the reaction of methane with active nitrogen would appear to give no information about the possible presence of two active species in active nitrogen.

Ethane

It is, perhaps, impossible to state categorically whether an induction effect is present or absent in the ethane – active nitrogen reaction. While a small

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induction has been drawn into some of the curves of Fig. 4, the magnitude of the effect is of the same order as the experimental error in determining the HCN yields from different experiments. (No attempt was made to establish the presence or absence of an induction by addition of hydrogen atoms, as in the experiments with methane, since such experiments are much more difficult and capable of less precision than those with a single discharge tube.) Since utmost care was taken with the experiments, it seems likely that an unequivocal result may not be possible with the present method of studying the reaction.

If second order rate constants are calculated for the different temperatures (2), and the Arrhenius lines plotted, the results of Fig. 4 lead, in both cases, to activation energies of approximately 2.7 and 6 kcal. in the temperature ranges -100°C. to about 150°C., and 150°C. to 475°C., respectively. The corresponding steric factors are of the order 10^{-4} and 10^{-2}.

The two activation energies may be attributed either to concomitant hydrogen atom reactions or to the presence of more than one chemically active species in active nitrogen. Of the two explanations, the first is probably to be preferred in view of the demonstrated effect of hydrogen atoms in the methane reaction.

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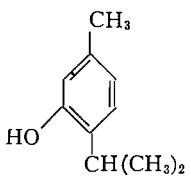
THE SYNTHESIS OF TWO ISOMERIC THYMOLS[1]

By R. A. B. Bannard and L. C. Leitch

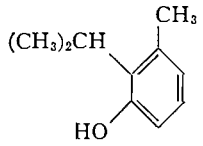
ABSTRACT

2-Isopropyl-3-methylphenol has been synthesized and found to be identical with the isopropyl-3-methylphenol of m.p. 69° C. obtained from the isopropylation of *m*-cresol. 6-Isopropyl-3-methoxytoluene has been synthesized and found to be identical with the methyl ether of the isopropyl-3-methylphenol of m.p. 112° C., also obtained from the isopropylation of *m*-cresol.

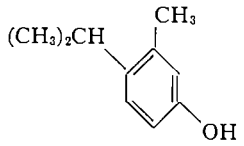
The alkylation of *m*-cresol with isopropyl alcohol in the presence of sulphuric acid reported by Chichibabine (4) and earlier workers gives, in addition to thymol (I), two isomers melting at 69° and 112° C. which were assigned the structures II and III respectively. On the basis of the orienting influences in



I



II

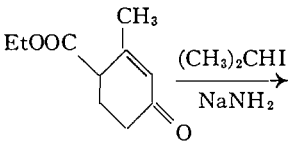


III

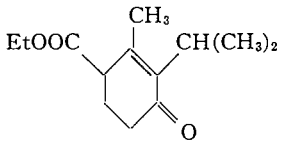
m-cresol and melting points, these formulae were probably correct. It seemed desirable, however, to confirm these structures either by degradation to known compounds or by independent synthesis.

The first course was not successful. All attempts to determine the location of the isopropyl group in II and III by oxidation of the methyl ethers to methoxyphthalic acids failed. The compounds were apparently completely oxidized by potassium permanganate as copious amounts of carbon dioxide were evolved on acidifying the reaction mixture and no organic compound could be isolated.

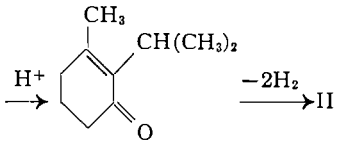
Alternatively, 2-isopropyl-3-methylphenol (II) was synthesized by the following reactions:



IV



V



VI

3-Methyl-4-carbethoxy-2-cyclohexene-1-one (IV), referred to as Hagemann's ester in the literature, was prepared from acetoacetic ester and trioxymethylene as described by Rouault and Smith (14). The sodio derivative of IV was

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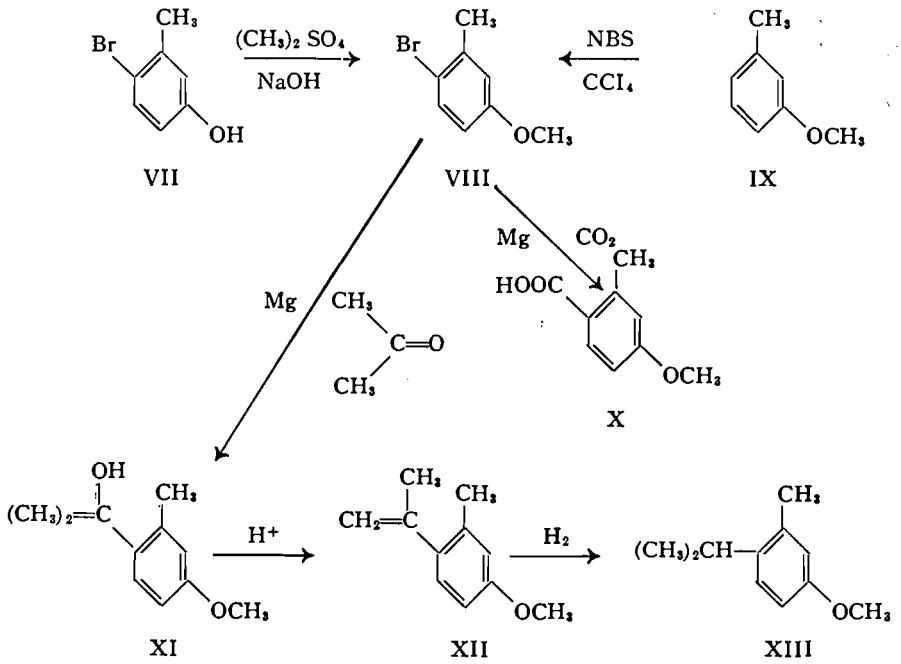
prepared from sodamide in liquid ammonia and alkylated therein with isopropyl iodide to 2-isopropyl-3-methyl-4-carbethoxy-2-cyclohexene-1-one (V) by the procedure of Horning, Horning, and Platt (10). Hydrolysis and decarboxylation of V as described by Horning, Denekas, and Field (9) gave 2-isopropyl-3-methyl-2-cyclohexene-1-one (VI). The semicarbazone of the ketone melted at 165–6° C. as reported by Dieckmann (7). Dehydrogenation of the ketone in mesitylene with palladized carbon according to the directions of Horning, Horning, and Walker (11) gave a small yield of a phenol, m.p. 68.5 to 69.5° C. Admixture of this compound with the isomer, m.p. 69–70° C., isolated from the isopropylation of *m*-cresol caused no depression in melting point. The infrared spectra of the two compounds were likewise identical. The structure II assigned to this isomer of thymol is therefore correct.

6-Isopropyl-3-methoxytoluene was in turn synthesized by the following sequence of reactions:



6-Bromo-3-methoxytoluene (VIII) was prepared in two ways: (*a*) by methylation of 3-methyl-4-bromophenol (VII) as described by Darzens and Levy (5); (*b*) by bromination of 3-methoxytoluene (IX) with N-bromosuccinimide by the procedure of Bannard and Latremouille (1). The orientation of the bromine atom in VIII upon which rests subsequent proof of the structure III was proved by Darzens and Levy (5) by converting the halide to 2-methyl-4-methoxybenzoic acid (X) via the Grignard reagent. The compounds obtained by the two routes were identical as shown by a comparison of their boiling points and refractive indices. Buu-Hoi (3) and Quelet and Paty (13) assigned

the same structure without proof to VIII prepared by bromination of 3-methoxytoluene (IX) with N-bromosuccinimide and bromine respectively.

The Grignard reagent prepared from 6-bromo-3-methoxytoluene (VIII) did not react with isopropyl bromide to give the expected 6-isopropyl-3-methoxytoluene. The result was surprising in view of the successful preparation of 6-*tert*-butyl-3-methoxytoluene from *tert*-butyl bromide and the same Grignard by Darzens and Levy (6). On treatment with acetone, however, the Grignard reagent gave a 45% yield of 2-(2-methyl-4-methoxyphenyl)-propanol-2 (XI) together with 38% of 6-isopropenyl-3-methoxytoluene (XII). The latter was undoubtedly formed by dehydration of the carbinol (XI) under the influence of iodine used to initiate the reaction. A similar instance has been reported recently by Edwards and Cashaw (8). 6-Isopropenyl-3-methoxytoluene was also obtained in 80% yield by dehydration of the carbinol (XI) with dilute sulphuric acid.

Hydrogenation of 6-isopropenyl-3-methoxytoluene (XII) with Adam's catalyst gave 92% of 6-isopropyl-3-methoxytoluene (XIII). Finally, methylation of the thymol isomer III yielded a product which has the same boiling point, refractive index, and infrared absorption spectrum as XIII. It must therefore be concluded that the isomer of m.p. 112° C. is 3-methyl-4-isopropylphenol.

EXPERIMENTAL*

A. Synthesis of 2-Isopropyl-3-methylphenol

3-Methyl-4-carbethoxy-2-cyclohexene-1-one (IV)

The ketoester was prepared in 40% yield by the directions of Rouault and Smith (14). After a small low-boiling fraction was collected, the pure ester distilled at 105–107° at 2 mm., n_D^{20} 1.4860.

2-Isopropyl-3-methyl-4-carbethoxy-2-cyclohexene-1-one (V)

For the alkylation of the ester IV the following modification of the method of Horning, Horning, and Platt (10) was used. The ketoester IV (25.7 gm., 0.14 mole) was added dropwise from a separatory funnel to sodamide prepared from 4.4 gm. of sodium and 125 ml. of liquid ammonia. The ammonia was allowed to evaporate during stirring and addition of 50 ml. of dry toluene. Isopropyl iodide (27.0 gm., 0.17 mole) was now added and the reaction mixture heated just below refluxing overnight. It was treated with a little ethanol and then poured into water. The toluene layer was washed with water and then dried over a small quantity of anhydrous calcium chloride. Most of the toluene was removed under 50 mm. pressure. The ester was then fractionated under 3 mm. in a small Vigreux column with total condensation – partial take-off still head. The main fraction of alkylated ketoester was collected between 115° and 119° C. at 3 mm. Yield: 15.0 gm. (60%), n_D^{20} 1.4868.

The semicarbazone separated from a solution of 1 gm. each of the ketoester, semicarbazide hydrochloride, and sodium acetate in dilute ethanol after it had been left to stand for a day. After one recrystallization from dilute ethanol–

**All melting points are uncorrected.*

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water the semicarbazone melted at 203–204° C. Calc. for $C_{14}H_{23}N_3O_3$: C, 59.75%; H, 8.24%; N, 14.94%. Found: C, 60.21%; H, 8.36%; N, 15.13%.

2-Isopropyl-3-methyl-2-cyclohexene-1-one (*VI*)

The ketoester V (14.0 gm.) was hydrolyzed and decarboxylated by treating it successively with alcoholic sodium hydroxide and sulphuric acid as reported by Horning, Denekas, and Field (9). Fractional distillation of the ketone after it had been washed and dried in ether gave 6.7 gm. of product, b.p. 94–97° C. at 14 mm., n_D^{20} 1.4888. The semicarbazone prepared as described above melted at 165–166° C. after one recrystallization from ethanol–water. Dieckmann (7) gives 167–168° C. as the melting point of the semicarbazone.

2-Isopropyl-3-methylphenol (*II*)

The dehydrogenation of VI was carried out as described by Horning, Horning, and Walker (11) except that the palladium adsorbed on carbon was prepared from palladium chloride (1.0 gm.), carbon black (10.0 gm.), and formaldehyde (12). Five grams of 2-isopropyl-3-methyl-2-cyclohexene-1-one (VI) was heated under reflux for two hours with 1.5 gm. of the dehydrogenation catalyst in 20 ml. of mesitylene. The supernatant liquid was decanted and extracted with 5% aqueous sodium hydroxide. On acidification of the aqueous extract a small amount of oily material which crystallized on being cooled and stirred was precipitated. It was taken up in pentane and crystallized therefrom on slow evaporation. The crystals melted at 68–69.5° C. The melting point was unchanged by admixture with the isomer of m.p. 69° isolated from the isopropylation of *m*-cresol.

B. Synthesis of 6-Isopropyl-3-methoxytoluene

3-Methoxytoluene (*IX*)

3-Methoxytoluene (IX) was prepared by the method of Ullmann and Uzbachian (15). Yield 70.0%, b.p. 61–63° C. at 10 mm., n_D^{20} 1.5123. The infrared spectrum of this substance was identical with that reported by Barnes *et al.* (2).

3-Methyl-4-bromophenol (*VII*)

3-Methyl-4-bromophenol (VII) was obtained in approximately 50% yield by the method of von Walther and Zipper (16). It melted at 62.5–63.5° C.; von Walther and Zipper (16) report m.p. 62° C.; Darzens and Levy (5), 63° C.

6-Bromo-3-methoxytoluene (*VIII*)

(*a*) *From 3-methyl-4-bromophenol* (*VII*).—3-Methyl-4-bromophenol (VII) (32.8 gm., 0.175 mole) was dissolved in 15% sodium hydroxide (40 cc.) in a 150 cc. beaker equipped with a teflon-covered magnetic stirring bar, thermometer, and burette. The stirred solution was treated at 40° C. with dimethyl to sulphate (45.0 gm., 0.357 mole) in one portion. The temperature rose rapidly to 87° C., and the solution turned acidic, became turbid, and separated into two layers. The mixture was treated with small portions of 15% sodium hydroxide (approximately 3 cc. per addition) until no further acidic reaction was evident

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(10 min., 36.5 cc.). Stirring was continued for a further 40 min. by which time the temperature had fallen to 35° C. The oily layer was taken up in ether (50 cc.), the aqueous phase extracted with ether (4×50 cc.), and the combined extracts dried over anhydrous magnesium sulphate (25 gm.). The ether solution was decanted, the ether removed by evaporation on the steam bath, and the residue distilled *in vacuo* yielding 18.1 gm. (51.4%) of 6-bromo-3-methoxytoluene (VIII) as a pale yellow oil, b.p. 104.5–106° C. at 10 mm., n_D^{20} 1.5609. (Quelet and Paty (13) report b.p. 111–112° C. at 15 mm., n_D^{20} 1.5593; Darzens and Levy (5) report b.p. 112° C. at 14 mm.) 4,6-Dibromo-3-methoxytoluene, 6.8 gm., m.p. 74–75° C., was obtained as by-product (Quelet and Paty (13) report m.p. 77° C.) together with 6.4 gm. of 3-methoxytoluene (IX).

(*b*) *From 3-methoxytoluene* (*IX*).—3-Methoxytoluene (IX) (61.0 gm., 0.500 mole) and carbon tetrachloride (80 cc.) were mixed in a 300-cc. round-bottomed flask and N-bromosuccinimide (89.0 gm., 0.500 mole) added in small portions. No evolution of heat occurred. The flask was fitted with a reflux condenser equipped with a calcium chloride guard-tube and the mixture heated by means of a "glascol" heating mantle. As soon as the solvent began to boil, a vigorous reaction occurred, making it necessary to replace the heating mantle by a cold water bath. After the initial vigorous reaction subsided, the mixture was heated under brisk reflux for six hours. The mixture was allowed to stand overnight and the precipitated succinimide removed by suction filtration and washed with carbon tetrachloride (3×20 cc.). The filtrate was concentrated by distillation at atmospheric pressure and the residue fractionated *in vacuo* yielding 89.0 gm. (88.1%) of 6-bromo-3-methoxytoluene (VIII) as a colorless oil, b.p. 104–105.5° C. at 10 mm., n_D^{20} 1.5610.

2-(2-Methyl-4-methoxyphenyl)-propanol-2 (*XI*)

A Grignard reagent was prepared in a conventional nitrogen-swept Grignard apparatus by addition of 6-bromo-3-methoxytoluene (VIII) (44.2 gm., 0.220 mole) in anhydrous ether (75 cc.) over a period of 3.5 hr. to magnesium turnings (4.86 gm., 0.200 gm-atom) covered with anhydrous ether (20 cc.) after the reaction had been initiated by addition of a small portion of the halide together with a crystal of iodine. The light brown reagent was heated under reflux for a further hour, then treated with a solution of acetone (11.6 gm., 0.200 mole) in anhydrous ether (15 cc.) over a period of 30 min. The reaction was exothermic and reflux was controlled by the rate of addition. Twenty minutes after the addition had been in progress the clear light brown solution deposited a pale yellow complex to form a very viscous mixture which became more fluid again by the time addition was complete. The mixture was heated under reflux for 15 min., allowed to stand overnight under nitrogen, and hydrolyzed by addition of saturated ammonium chloride solution (30 cc.) over a period of 30 min. The pale yellow solution was separated from the granular colorless solid by filtration and the latter washed with anhydrous ether (4×50 cc.). The combined filtrate and washings were dried over anhydrous magnesium sulphate (15 gm.). The ether solution was decanted and the drying agent washed with anhydrous ether (4×50 cc.). The ether was re-

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moved by heating on the steam bath and the residue was distilled *in vacuo* yielding 28.4 gm. of a mixture of oil and crystals, b.p. 100–130° C. at 10 mm. Separation of the crystals by filtration and further purification by recrystallization from 60–70° petroleum ether gave 16.2 gm. (45.0%) of 2-(2-methyl-4-methoxyphenyl)-propanol-2 (XI), m.p. 66–67° C. Calc. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95%. Found: C, 73.73; H, 9.03%. The infrared spectrum of this substance showed strong hydroxyl absorption at 3.0 μ.

The residual oil, 12.2 gm. (38.0%), n_D^{25} 1.5237, b.p. 99–102° C. at 11 mm., was subsequently identified as 6-isopropenyl-3-methoxytoluene (XII).

6-Isopropenyl-3-methoxytoluene (XII)

2-(2-Methyl-4-methoxyphenyl)-propanol-2 (XI) (5.40 gm., 0.0300 mole) and 90% sulphuric acid (10 cc.) were placed in a 35-cc. round-bottomed flask equipped with a teflon-covered magnetic stirring bar and reflux condenser. The mixture was heated under reflux with stirring for six hours, cooled, and extracted with peroxide-free ether (4×10 cc.). The ether extract was washed with 5% sodium bicarbonate solution (10 cc.), then with water (2×10 cc.), and dried over anhydrous magnesium sulphate (5 gm.). The ether solution was decanted and the desiccant washed with anhydrous ether (4×10 cc.). The solutions were combined and concentrated by distillation on the steam bath. The residue was transferred to a 10-cc. pear-shaped modified Claisen flask and distilled *in vacuo* yielding 3.92 gm. (80.8%) of 6-isopropenyl-3-methoxytoluene (XII) as a colorless oil, b.p. 94.5° C. at 9 mm., n_D^{25} 1.5243. Calc. for $C_{11}H_{14}O$: C, 81.45; H, 8.70%. Found: C, 81.27; H, 8.83%. The infrared spectrum of this substance showed strong terminal methylene group absorption at 11.1 μ which disappeared on hydrogenation.

6-Isopropyl-3-methoxytoluene (XIII)

(*a*) *From 6-isopropenyl-3-methoxytoluene (XII).*—6-Isopropenyl-3-methoxytoluene (XII) (5.45 gm., 0.0336 mole) was placed in the reaction flask of a hydrogenator together with Adams' Catalyst (0.200 gm.) and absolute ethanol (100 cc.) and hydrogenated at atmospheric pressure. The reaction was complete in 13 min. The mixture was filtered to remove the catalyst, and the ethanol removed from the filtrate by distillation *in vacuo*. The residue was dissolved in anhydrous ether (50 cc.) and dried overnight over anhydrous magnesium sulphate (3 gm.). The orange solution was decanted and the desiccant washed with anhydrous ether (4×10 cc.). The combined ether solutions were evaporated on the steam bath, transferred to a 10-cc. pear-shaped modified Claisen flask, and distilled *in vacuo* yielding 5.09 gm. (92.3%) of colorless to amber colored oil, b.p. 98° C. at 9 mm., n_D^{25} 1.5081.

(*b*) *From 3-methyl-4-isopropylphenol (III).*—3-Methyl-4-isopropylphenol (III) (15.0 gm., 0.100 mole), m.p. 112–113° C., obtained from the isopropylation of *m*-cresol (4) was dissolved in 15% sodium hydroxide solution (25 cc.) in a 100-cc. beaker equipped with a teflon-covered magnetic stirring bar, burette, and thermometer. The stirred solution was treated at 40° C. with dimethyl sulphate (25.2 gm., 0.200 mole) added in one portion. The tempera-

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ture rose rapidly to 82° C. and the solution became acidic and turbid and then separated into two layers. The mixture was treated with small portions (approximately 3 cc. per addition) of 15% sodium hydroxide until no further acidic reaction was evident (11 min., 18 cc.). The mixture was stirred for a further 30 min., transferred to a separatory funnel containing peroxide-free ether (25 cc.), and the ether layer separated. The aqueous phase was extracted with ether (3×25 cc.) and the combined ether solutions dried over magnesium sulphate (10 gm.). The ether solution was decanted, the desiccant washed with anhydrous ether (4×10 cc.), and the ether removed by evaporation on the steam bath. The residue was transferred to a 25-cc. pear-shaped modified Claisen flask and distilled *in vacuo* yielding 14.9 gm. (90.7%) of 6-isopropyl-3-methoxytoluene (XII) as a colorless oil, b.p. 98° C. at 9 mm., n_D^{25} 1.5083. Calc. for $C_{11}H_{16}O$: C, 80.46; H, 9.82%. Found: C, 80.56%; H, 9.90%. The infrared spectra of the 6-isopropyl-3-methoxytoluene (XIII) from 6-isopropenyl-3-methoxytoluene (XII) and from the isopropyl-3-methylphenol of m.p. 112–113° C. were measured as liquid films and found to be identical.

ACKNOWLEDGMENTS

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ETHYLENE DIAMINE TETRAACETIC ACID AND CITRIC ACID AS ELUANTS IN ION EXCHANGE SEPARATION OF RARE EARTHS[1]

By F. W. Cornish,[2] G. Phillips, and A. Thomas

ABSTRACT

Studies of the distribution of rare earths between the cation exchange resin Zeokarb 225 and solutions of ethylene diamine tetraacetic acid (EDTA) show the existence of large separation factors between members of this series. However, column experiments show that the separation is poorer than with citric acid, probably because of a slow process occurring in the solution. The variation of column efficiency with distribution coefficient has been examined. Elution of europium with citric acid appears to be diffusion controlled, while that with EDTA is not. Further experiments with strontium indicate that its elution with both EDTA and citric acid is diffusion controlled. The results are in general agreement with Glueckauf's equation relating column variables with the height equivalent to a theoretical plate. Column irregularities appear to account for the very low diffusion constants calculated from this relation.

INTRODUCTION

Ordinary cation exchange resins are sufficiently selective to allow the separation of two cations possessing somewhat different ionic potentials by successive equilibration with a third ion. In the case of ions of the same charge and almost identical radii, e.g. the rare earths, the differences are so small that an almost impossibly large number of equilibrations would be required for complete separation. The effective selectivity can be increased by using complexing agents; in this way the ion which is least adsorbed by the resin undergoes the greatest complexing in the aqueous phase. Much of the selectivity under these conditions can be attributed to the complexing agents, making their choice of considerable importance. In the absence of any theory regarding the selection of such reagents it was thought that a very strongly complexing species might be expected to exaggerate the slight differences of basicity which exist between members of the rare-earth series. The distribution of rare earths between solutions of ethylene diamine tetraacetic acid (EDTA) and the cation exchanger Zeokarb 225 was therefore investigated.

The chromatographic technique employed in ion exchange separations depends on the quantities to be separated and the purity required. Large quantities are best separated by 'break through' or band displacement techniques. Several papers describing this approach using solutions of complexones have been published (4). Such methods always lead to overlapping of the bands, only a part of any one species being obtained 100% pure. Nevertheless tens or hundreds of grams can be adequately handled. Small quantities, of the order of a few milligrams, are best separated by the band elution technique, which under the correct conditions can lead to virtually total recovery of completely pure materials. The elution of traces of rare earths and strontium

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by solutions of citrate and EDTA is examined in the present work in terms of the column variables.

The distribution coefficient (K_d) between solution and resin is given by (12)

$$[1] \qquad K_d = \frac{(\text{quantity adsorbed on resin})(\text{volume of solution})}{(\text{quantity in solution})(\text{mass of resin})} .$$

When the amount of solute adsorbed by the resin is less than about 2% of the resin capacity K_d is almost independent of solute concentration. Under these conditions the material is eluted from a column in an almost symmetrical peak (approximately a normal error curve, Fig. 1). Tompkins and Mayer

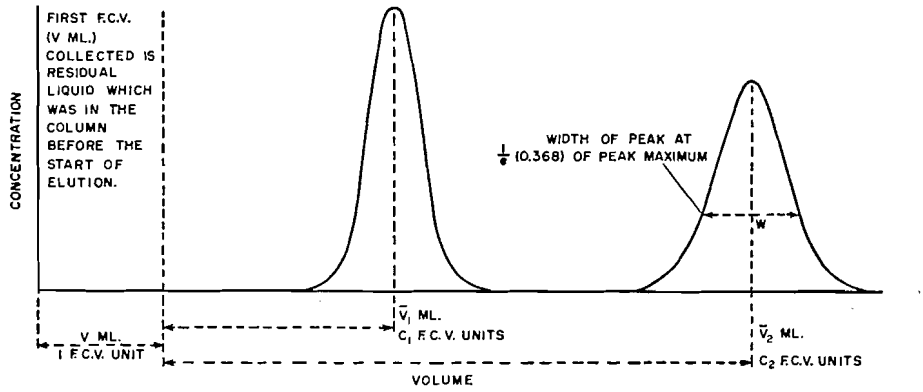

FIG. 1. Illustration of notation.

(13) have shown that the number of free column volumes of eluant required to elute the maximum of a peak is given by

$$[2] \qquad C = \bar{v}/v = K_d(\text{mass of resin in column})/v$$

where $\bar{v}$ has the significance shown in Fig. 1. The free column volume, v, is the total volume of the resin bed, v_T, less the volume of the resin. The bed distribution coefficient (K_b) is defined as

$$[3] \qquad K_b = \frac{(\text{amount of solute adsorbed per ml. of bed})}{(\text{amount of solute per ml. of solution})} .$$

This is identical with the D used by Kraus and Moore (8) and the K_d used by Glueckauf (5, 6). It can be shown that $K_b = fC$ where f is the fractional bed void, i.e. $f = v/v_T$. The degree of separation of two solutes by elution depends on the separation between peak maxima; a measure of this is given by the ratio of volumes required to elute each peak maximum, i.e. $\bar{v}_2/\bar{v}_1$ in Fig. 1. From above $\bar{v}_2/\bar{v}_1 = C_2/C_1 = K_{d_2}/K_{d_1} = K_{b_2}/K_{b_1}$ = the separation factor, α; this can be determined from equilibrium studies and is highly dependent on the complexing agent employed.

The degree of separation also depends on the widths of the eluted peaks. The physical parameters of the column system, e.g. flow rate and particle

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size, usually exert more control on the width of the peak than does the complexing agent. In the present work the number of theoretical plates associated with an elution is derived from (5, 6)

$$N = 8(v+\bar{v})^2/w^2 \quad [4]$$

where w is the width of the eluted peak at $1/e$ (0.368) of its maximum height in the same units as v and $\bar{v}$. The efficiency of a column elution can be measured in terms of the theoretical plates, for a greater number of equilibrium stages yields narrower peaks and therefore less overlapping.

EXPERIMENTAL

Equilibrium Distribution Experiments

These experiments were carried out by equilibrating known weights of resin with known volumes of solution containing 0.005 *M* EDTA, 0.14 *M* acetic acid, and a small amount of radioactive rare earth. Measurement of the radioactivity in the solution before and after equilibration furnished the data to calculate K_d from equation [1].

The resin, Zeokarb 225 (about 8% cross linked), a high capacity sulphonic acid type, was dry sieved 240–300 B.S.S. mesh. After 'fines' were removed by decantation it was washed several times with 3 *M* HCl and 3 *M* NH_4Cl solutions. A stock of this resin in the H^+ form was air dried and kept in a tightly stoppered bottle. By drying to constant weight at 105°C. it was found that the weight of air-dried resin was 1.51 times the weight of oven-dried resin.

Most of the radioactive tracers were obtained by thermal neutron irradiation of 'Specpure' rare-earth oxides; earlier experiments had shown the amount of contaminating activities to be negligible. The Ce^{144} was obtained from fission products. Experiments with dysprosium were performed with inactive material; the required concentrations were determined by a comparative radioactivation procedure involving the counting of solutions containing the 2.32 hr. Dy^{165}. The rare earths were stored as chlorides in dilute HCl solution.

Since EDTA is only slightly soluble at hydrogen ion concentrations required for reasonable K_d's, acetic acid was added to provide greater buffering capacity. This is of considerable importance if attempts are made to separate all the rare earths by eluting with solutions of progressively higher pH values. A stock solution was prepared by dissolving a weighed quantity of EDTA in boiling water with the minimum of concentrated ammonia, diluting to the required volume, adding glacial acetic acid, and adjusting the pH with concentrated ammonia. Free EDTA slowly crystallizes from this solution at pH < 2.94. In order to preclude the presence of Cl^- ions (and hence associated NH_4^+ ions) the following procedure was adopted. The rare earth was adsorbed onto a small column of Zeokarb in the NH_4^+ form. After it had been washed with water it was eluted from the column with stock EDTA at pH 5. This eluate was mixed with stock EDTA at pH 3.5 to yield a rare-earth concentration of about 10^{-7} to 10^{-5} *M*. The pH was finally adjusted to between 4.5 and

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5.0 with concentrated ammonia. Various known weights of air-dried resin (0.5 to 1.5 gm.) in the H^+ form were shaken with 15 ml. aliquots of this solution for 48 hr. This had been found to be ample time for equilibrium to be attained. The EDTA – rare earth stock and the final equilibrated solutions were analyzed by evaporating known weights on aluminum trays and β–γ counting with an end-window Geiger counter. Corrections for decay, dead time, and background were made where necessary. Measurements of pH were made with a 'Cambridge' bench type glass electrode assembly calibrated at pH 4.00 with 0.05 M potassium hydrogen phthalate. All experiments were carried out at room temperature.

The results for neodymium, typical of those for other rare earths, are shown in Table I. K_d values calculated from equation [1] on the basis of oven-dried

TABLE I

DISTRIBUTION OF NEODYMIUM BETWEEN 0.005 M EDTA PLUS 0.14 M ACETATE AND ZEOKARB 225 AS A FUNCTION OF pH AT 23°C.
Initial volume of solution = 15.0 ml.
Initial activity of stock solution = 3778 counts/min./gm.
Initial concentration of neodymium = 9×10^{-8} M

Weight of air-dried resin, gm.	Equilibrated solution		K_d	Corrected K_d
	counts/min./gm.	pH		
0.505	3910	4.33	0	0
0.533	3810	4.31	0	0
0.584	3940	4.28	0	0
0.613	3821	4.24	0	0
0.612	3800	4.24	0	0
0.679	3844	4.18	0	0
0.766	3636	4.11	1.1	1.9
0.805	3526	4.08	2.0	2.8
0.823	3386	4.05	3.2	3.9
0.860	3224	4.02	4.5	5.3
0.937	2776	3.94	8.7	9.5
1.003	1990	3.86	20.2	21
1.096	1230	3.74	42.6	45
1.159	588	3.63	105	108
1.291	198	3.48	322	324

resin are given in column 4. Above pH 4.11 the concentration of rare earth in solution after equilibration (counts/min./gm.) is slightly larger than for the original stock. If it is assumed that this occurs because of absorption of pure water by the originally air-dried resin, then it can be calculated that 1 gm. of air-dried resin absorbs about 0.5 gm. of water. Hence, a 'true' value for the volume of solution and a 'true' initial concentration can be obtained for each experiment. K_d's calculated from equation [1] using these 'true' values and weights of oven-dried resin are given in column 5. All the results are summarized in Fig. 2; rare earths not examined are represented by broken lines.

Column Experiments

Elutions were carried out at room temperature and at 80°C. from columns of Zeokarb 225 using both EDTA and citric acid solutions. At room temperature europium and strontium were eluted separately; at 80°C. a mixture of

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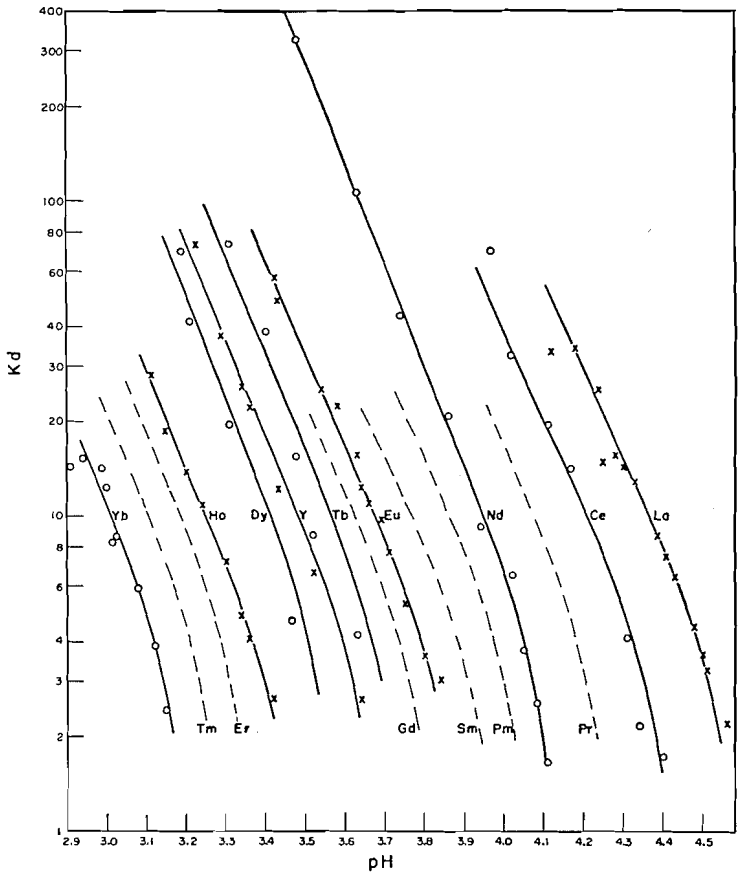

FIG. 2. Variation of distribution coefficient of rare earths between 0.005 *M* EDTA+0.14 *M* acetate and Zeokarb 225 as a function of pH.

lanthanum, cerium, and praseodymium was separated. In all cases β–γ active tracers were used and elutions were followed by measuring the radioactivity.

The Zeokarb 225 was wet-sieved in the NH_4^+ form to give a fraction which passed through a 300 B.S.S. sieve. The largest particles were selected from this fraction by repeated decantation, only those settling through 1 ft. of water in 40 min. being collected. Since 300 mesh corresponds to a particle radius of 0.0027 cm. the particles selected by decantation were estimated to have a mean radius of 0.0019 cm. This material was washed several times with 5 *M* HCl, then with slightly alkaline ammonium citrate solution, and finally with distilled water. The same batch of resin was used in all experiments.

Experiments at 80° were performed with a column 124 cm. × 0.23 sq. cm. supported on a small pad of cotton wool. The temperature was maintained by refluxing alcohol in a surrounding jacket. A 6-ft. head of eluant was necessary to attain a flow rate of 0.069 ml./min. The effluent was passed through a short length of capillary tubing to a 2.5 cm. diameter planar spiral of thin-walled glass of internal diameter about 0.08 cm. and total volume 0.4 ml. This spiral

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was held between two thin end-window Geiger tubes connected in parallel and mounted in a lead castle. Pulses from the Geiger tubes were fed to a ratemeter with a time constant of 10 sec. whose output was recorded continuously as a function of time.

Columns 40 cm. $\times$ 1.0 sq. cm. were used for experiments at room temperature. The resin bed rested on a small pad of cotton wool nestling in the join of the glass tube with a 2 in. piece of capillary tubing. Solutions were fed in from a one liter separating funnel, and heads of between 6 in. and 5 ft. provided the different flow rates used.

All columns were packed by pouring an aqueous slurry of the resin into the column tubes which were already half full of water. The resin was allowed to settle freely, while the tubes were gently tapped at frequent intervals to assist close packing.

Before an experiment was begun the column was washed with the eluant until the pH of effluent and eluant were identical. It was then washed with water. Two separate portions of resin were removed from the top of the column, each having a settled volume of 0.5 ml. The active material was adsorbed onto one of these portions from dilute acid solution. It was then washed with a 0.5 M solution of ammonium chloride having a pH such that any resin in equilibrium with it would have the same $[\overline{NH_4^+}]/[\bar{H}^+]$ ratio as would resin in equilibrium with the eluant. (This ammonium chloride solution was obtained by passing a 0.5 M solution of ammonium chloride through a separate bed of resin which had been exhaustively washed with the eluant.) The resin bearing the tracer was washed with water and then gently slurried on top of the column and allowed to settle, the original resin–water interface at the top of the column having first been made horizontal. The other 0.5 ml. portion of resin was carefully slurried on top, thus providing a protective layer over the tracer-carrying resin. After the water above the resin level had been removed the eluant was very carefully introduced to start the elution.

The position and nature of the eluted bands were obtained (*a*) at 80°C. by monitoring the spiral as described above, (*b*) at room temperature by using the spiral and by collecting each drop on a separate aluminum tray, evaporating to dryness, and counting each tray with a Geiger counter. Both methods gave the same result for the number of theoretical plates associated with any one elution. The free column volumes, v, were measured by determining the volumes of water required to wash through a small amount of the β–γ active I^{131} as iodide ion.

The activity in the eluant versus volume (or time) followed bell-shaped, symmetrical curves in the case of elutions with citrate and for elution of strontium with EDTA. Elution of rare earths with EDTA led to bell-shaped peaks which were relatively flatter and always had a drawn-out tail. This tail was much less pronounced at 80°C. Separations of Pr, Ce, and La at 80°C. are shown in Fig. 3. Results of other elutions are summarized in terms of theoretical plates, this number being calculated from equation [4].

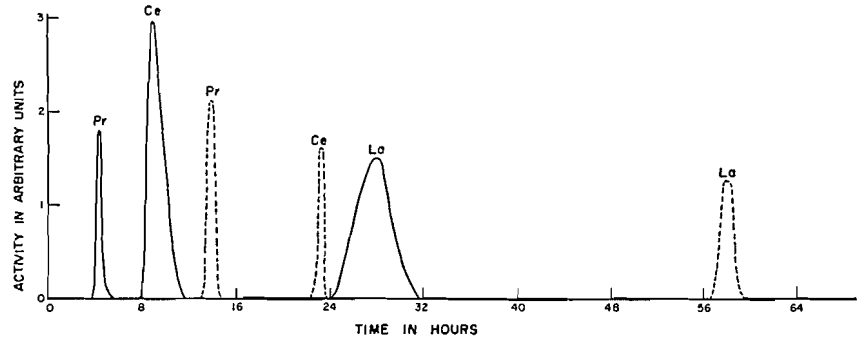

FIG. 3. Elution of 10^{-4} gm. cerium, 10^{-4} gm. praseodymium, and 10^{-6} gm. lanthanum from a column of Zeokarb 225 (particle radius = 0.0019 cm.), length 124 cm., area 0.23 sq. cm. at a flow rate of 0.069 ml./min. at 80°C. —0.005 *M* EDTA+0.14 *M* acetate, pH 4.26; ----5% citrate, pH 3.65.

DISCUSSION

Fig. 2 shows the range of pH values over which EDTA solutions could be useful in cation exchange elution. Since the principal complexing species (10) over this range is H_2Y^{2-} (where H_4Y = EDTA) the equilibria involved are probably

$$M^{3+}+H_2Y^{2-} \rightleftharpoons MY^{-}+2H^{+}, \quad [5]$$

$$M^{3+}+3NH_4R \rightleftharpoons MR_3+3NH_4^{+}, \quad [6]$$

where R denotes an equivalent of resin anion and M^{3+} denotes the trivalent rare-earth ion. An accurate analysis of the results in terms of these equilibria is not possible owing to the large increase of ammonium ion concentration (and hence ionic strength) with pH. This accounts for the slightly non-linear nature of the curves in Fig. 2. By using calculated activity coefficients for the aqueous components and assuming that the activity coefficient of the metal ion on the resin is a constant, the results have been compared with predictions from equations [5] and [6]. If the number of H^+ ions involved in equation [5] is used as a parameter the data for each rare earth can be fitted by using values of this parameter between the extremes of 1.7 (Nd) and 2.4 (Ho). Since the complexing of rare earths by EDTA in this pH region is known to involve the liberation of two hydrogen ions (15) the above equations appear to offer a reasonable explanation of the observed distributions. The sequence of curves (Fig. 2) follows the sequence of atomic numbers. The quasi rare earth yttrium behaves with an apparent atomic number of 65.5. This is in accord with known complexity constants (15), although Vickery (14) places yttrium between dysprosium and erbium. Comparison of values of $\alpha(=K_{d_2}/K_{d_1})$ for any two rare earths with similar data for the citrate – Dowex 50 system (12) shows that a greater separation factor is to be expected in one equilibrium stage by using EDTA. Thus, in Fig. 3 the ratios of times to reach peak maxima for any pair of rare earths are higher for the elution with complexone than for the corresponding citrate separation. Data presented

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by Mayer and Freiling (9) also show that EDTA offers greater separation factors than citric, lactic, and glycollic acids.

The number of theoretical plates is a measure of the effective number of equilibrium stages brought about by the non-equilibrium process of elution. The number of plates, and hence the degree of separation, is therefore controlled by the extent of equilibration in any section of the column. Earlier work has shown that the speed of ion exchange reactions is limited by diffusion of the participating species and not by the actual ion exchange process (1). The extent of equilibration in any horizontal slice of the column will therefore depend on the time spent by the solute in the slice. This time is directly related to K_b and the flow rate. At constant flow rate the number of plates should increase with K_b and tend to a limiting value at high K_b. This qualitative conclusion is borne out by the Sr–citrate, Sr–EDTA, and Eu–citrate experiments (Fig. 4). For such diffusion controlled elutions Glueckauf (5) has developed the following theoretical relation:

$$[7] \qquad HETP = 1.64r + \frac{K_b}{(K_b+f)^2}\frac{0.142r^2\bar{F}}{D_S} + \left(\frac{K_b}{K_b+f}\right)^2 \frac{0.266r^2\bar{F}}{(1+70r\bar{F})D_L}$$

where $HETP \equiv$ height equivalent to a theoretical plate = length of column/N, r = particle radius, $\bar{F}$ = linear flow rate (ml. sq. cm./sec.), f = fractional bed void. The first term represents the theoretical minimum of the $HETP$ and arises from the finite size of the resin particles. The other terms represent contributions due to (*a*) diffusion within the resin particle (diffusion constant D_S) and (*b*) diffusion through the immobile liquid film pictured as surrounding each resin particle (diffusion constant D_L). For low values of K_b diffusion through the resin accounts for the greater part of the diffusion contribution to the $HETP$. The opposite is true for high values of K_b. The full lines in Fig. 4 were calculated from equation [7] using the following values of D_S and D_L (in cm.^{2} sec.$^{-1}$).

	D_S	D_L
Europium (citrate elution)	1.7×10^{-8}	1.7×10^{-7}
Strontium (both citrate and EDTA elution)	2.7×10^{-8}	4.4×10^{-7}

In the present experiment $(70r\bar{F}) \ll 1$ so that with both K_b and r constant $HETP$ is a linear function of $\bar{F}$ (Fig. 5). The slopes of these lines from the experimental points (0.23 ($K_b = 3$) and 0.37 cm.$^{-2}$ min.$^{-1}$ ($K_b = 0.6$)) are in good agreement with those calculated from equation [7] using the values of D_S and D_L given above (0.21 and 0.37 cm.$^{-2}$ min.$^{-1}$ respectively). Further, the intercept at $\bar{F} = 0$ is close to $1.64r$ as required by equation [7]. However, despite this apparent agreement the diffusion constants are much smaller than might be expected. Thus Boyd and Soldano (3) find a diffusion constant of 2.2×10^{-7} cm.^{2} sec.$^{-1}$ for La^{3+}–Na^+ exchange in an 8% cross-linked sulphonic acid resin at 25°C.; D_S for the Eu–citrate experiments, in which D_S refers to Eu^{3+}–NH_4^+ exchange in the resin, is 10-fold smaller. Again D_L might be

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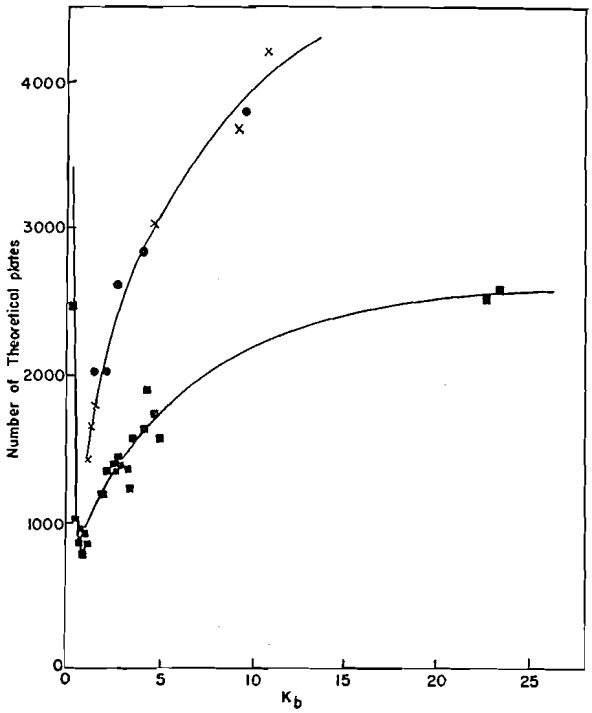

FIG. 4. Variation of number of theoretical plates with K_b using a column of Zeokarb 225 (particle radius = 0.0019 cm.), length 37 cm., area 1.0 sq. cm. at a flow rate of 0.10 ml./min. at room temperature. × elution of 10^{-6} gm. strontium with 0.10 *M* EDTA+0.5 *M* acetate; ● elution of 10^{-6} strontium with 5% citrate; ■ elution of 0.015 mgm. of europium with 5% citrate.

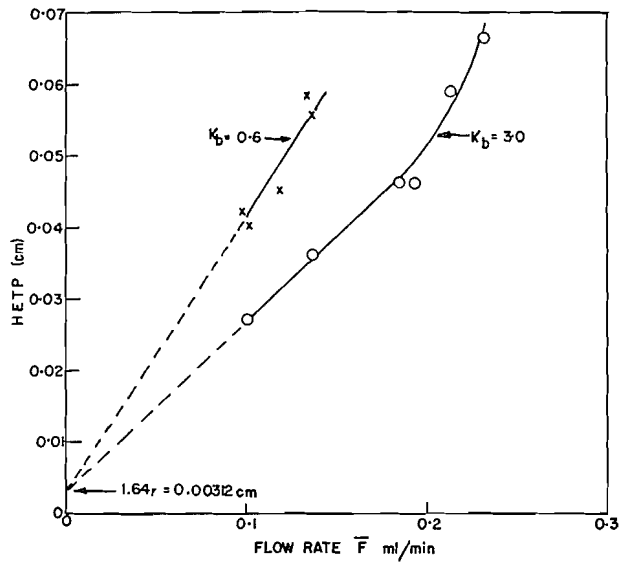

FIG. 5. Variation of *HETP* with flow rate for elution of 10^{-5} gm. of europium from a column of Zeokarb 225 (particle radius 0.0019 cm.), length 37 cm., area 1.0 sq. cm. with 5% citrate at room temperature.

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expected to be about one third of the diffusion constants for the simple hydrated ions at infinite dilution because (*a*) the diffusing species are probably complexes, and (*b*) the ionic strength is high. On this basis we predict for the europium experiments $D_L \sim 2\times10^{-6}$, and for the strontium experiments $D_L \sim 3\times10^{-6}$ cm.^{2} sec.$^{-1}$. These higher values of the diffusion parameters can be incorporated into equation [7] by assuming the first term to be too small. This is not unreasonable since this term must allow for any disturbances due to channelling, turbulence, as well as finite particle size (2). It should be pointed out that for the present experimental conditions the diffusional terms contribute considerably less to the *HETP* than the 'imperfections' term, which up to $\bar{F} \sim 0.2$ cm. min.$^{-1}$ must have the form "constant $+\phi\bar{F}$" where ϕ is a function of K_b and r.

An interesting feature arises when K_b is very small. For $K_b < 0.3$ the apparent number of plates increases rapidly becoming, ideally, (length of column)/1.64r at $K_b = 0$. This rise is 'false' in that very little interaction with the resin occurs; on the other hand it expresses the fact that the peak is very narrow. If the equation $N = 8\bar{v}(\bar{v}+v)/w^2$ were to be used (11), N would continue falling as K_b decreased from 0.3 becoming $N = 0$ at $K_b = 0$. While this would express the idea that the number of 'true' theoretical plates (i.e. equilibrations with the resin) is very small the use of such low values of N in cross-contamination calculations would lead to erroneously high results.

The decision to buffer the EDTA solutions with 0.42 *M* acetate was based on the results shown in Fig. 6. Despite this buffering, elution of europium with EDTA at room temperature invariably resulted in a small number of theoretical plates. The form of the variation of N with K_b at different EDTA concentrations is surprising (Fig. 7). The peak at $K_b = 1.3$ for 0.0125 *M* EDTA was reproducible although the precision in any single experiment was low. From these results it appears that the peak in the N versus K_b curve may move to a lower K_b with decreasing EDTA concentration. Low values for N were persistently obtained when eluting lutecium and when various concentrations of ammonium chloride were present in the eluting agent. It should be emphasized that these experiments involved the calculation of N from quite asymmetrical elution curves. Nevertheless the absence of a smooth variation of N with K_b suggests that diffusion is not the controlling feature. It seems possible that some slow chemical step occurs in the solution phase. This is supported by the observed slow exchange of ferric ions with the ferric–EDTA complex in aqueous solution (7). It was found that equilibrium was approached more slowly in the Eu–EDTA system than with Sr–EDTA, Sr–citrate, and Eu–citrate. The peak in the N versus K_b curve may perhaps be attributed to some fortunate combination of the rate determining factors. The number of theoretical plates would still be expected to increase with temperature. At 80°C. the rare earth – EDTA peaks are nearly symmetrical (Fig. 3) but the number of theoretical plates is still below that of corresponding citrate elutions (Table II). The calculated cross contamination (6) between lanthanum and cerium in Fig. 3 is slightly greater for EDTA than for citrate elution. It appears therefore that EDTA is somewhat inferior to citrate for the separation of traces of rare earths by ion exchange elution.

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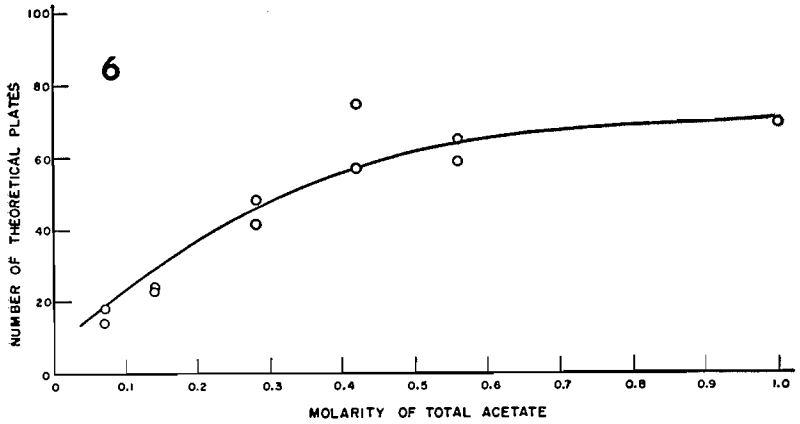

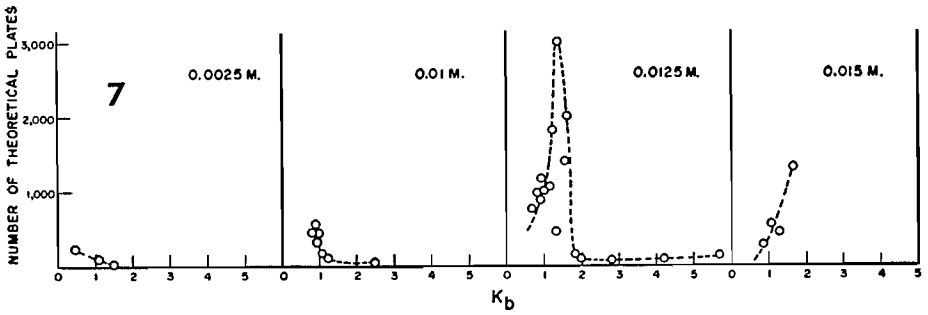

FIG. 6. Variation of number of theoretical plates with concentration of total acetate for elution of 10^{-5} gm. of europium from a column of Zeokarb 225 (particle radius 0.0019 cm.), length 40 cm., area 0.9 sq. cm. at a flow rate 0.10 ml./min. at room temperature with 0.005 *M* EDTA plus the concentration of total acetate shown.

FIG. 7. Variation of number of theoretical plates with EDTA concentration for elution of 10^{-5} gm. europium from a column of Zeokarb 225 (particle radius 0.0019 cm.), length 40 cm., area 0.9 sq. cm. at a flow rate of 0.10 ml./min., with 0.42 *M* total acetate plus the concentration of EDTA shown.

TABLE II

ELUTION OF TRACES OF PR, CE, AND LA FROM COLUMN OF ZEOKARB 225 (PARTICLE RADIUS = 0.0019 CM.), LENGTH 124 CM., AREA 0.23 SQ. CM., WITH EITHER 5% CITRATE OR 0.005 *M* EDTA PLUS 0.42 *M* ACETATE, FLOW RATE 0.3 ML./SQ. CM./MIN. AT 80°C.

Solution	Pr		Ce		La		Ratio of K_b's	
	K_b	*N*	K_b	*N*	K_b	*N*	Ce/Pr	La/Ce
EDTA pH 4.26	0.45	609	0.90	945	2.7	1270	2.0	3.2
EDTA pH 4.28	0.36	1005	0.85	410	3.2	470	2.4	3.8
Citrate pH 3.65	1.43	4750	2.7	7100	4.3	9550	1.9	2.7
Citrate pH 3.65	1.27	5520	—	—	6.3	6000	—	—

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THE SURFACE ENERGIES OF AMORPHOUS SILICA AND HYDROUS AMORPHOUS SILICA[1]

By Stephen Brunauer, D. L. Kantro, and C. H. Weise

ABSTRACT

The total surface energies (or, more strictly, surface enthalpies) of amorphous silica and hydrous amorphous silica were determined by measuring the heats of solution in a mixture of nitric acid and hydrofluoric acid of samples having differing specific surface areas and bound water contents, and by measuring the surface areas by the B.E.T. method, using nitrogen as adsorbate. The molecular area of nitrogen was taken to be 16.2 Å^2 at 77.3°K. The surface energy of amorphous silica of zero water content (or the energy of the pure siloxane surface) at 23°C. was found to be 259±3 ergs/cm.^{2} The heat of hydration by liquid water of the siloxane surface to silanol surface at 23°C. was found to be 258.6±13.0 cal./gm. of water. From these two values, with the added assumption that the molecular area of bound water was 25 Å^2, the surface energy of hydrous amorphous silica with a completely hydrated surface (or the energy of pure silanol surface) at 23°C. was calculated to be 129±8 ergs/cm.^{2} This value is only slightly greater than the surface energy of liquid water. Surface area determinations were also made by water vapor adsorption at 25°C. The packing of physically adsorbed water appeared to be determined by the geometry of the surface. The cross-sectional area of the adsorbed water molecule was found to be 12.5 Å^2. The density of amorphous anhydrous silica was 2.28 to 2.29 gm./cc. Silica particles having an average dimension of 37 Å were dehydrated at lower temperatures and sintered at lower temperatures than particles having an average dimension of 64 Å.

INTRODUCTION

The investigations described in this paper were preceded by an attempt to determine the surface energies of calcium silicate hydrates. The calcium silicate hydrates obtained in the hydration of tricalcium silicate, β-dicalcium silicate, and portland cements are colloids; consequently, the specific surface areas and surface energies of the hydrates play vital roles in determining many of their important structural characteristics. Powers and Brownyard (16) demonstrated highly significant correlations between the specific surface areas of hardened portland cement pastes and strength, shrinking and swelling, permeability to water, and freezing of water and thawing of ice in the pores. Until recently, no work has been done on the surface energies of the colloids constituting the most important parts of hydrated calcium silicates and portland cements. This is not surprising, because very little work has been done on the surface energies of solids, in general.

The first experiments on the surface energies of afwillite and tobermorite, the calcium silicate hydrates obtained in the hydration of tricalcium silicate at room temperature (2), revealed the complexity of the system and the difficulty of the problem. It appeared desirable, therefore, to investigate the surface energies of simpler, closely related compounds, such as calcium oxide, calcium hydroxide, amorphous silica, and hydrous amorphous silica. The results on the first two compounds were reported before (4); those on the last two are reported here.

[1]*Manuscript received June 6, 1956.*
Contribution from the Portland Cement Association, Research and Development Laboratories, Chicago, Illinois.

There is no experimental value in the literature for the surface energy of any of the crystalline varieties of silica. Several theoretical calculations were made for quartz, which were listed by Axelson and Piret (1). The surface energy values ranged from 510 to 2300 ergs/cm.^{2}; Axelson and Piret adopted the value of 980 ergs/cm.^{2}

Shartsis and Spinner (17) determined the surface tensions of molten alkali silicates and, by extrapolating to zero alkali content, they concluded that the surface tension of vitreous silica at 1300°C. was of the order of 300 dynes/cm. Noting that the temperature coefficient of the surface tension had been found to be small, Iler and Yates (11) estimated the surface energy of vitreous silica at room temperature to be 275 ± 25 ergs/cm.^{2}

In the present investigations, the surface energies (or, more strictly, surface enthalpies) of amorphous silica and hydrous amorphous silica were determined by measuring the heats of solution of samples having differing surface areas and bound water contents, and by measuring the surface areas by nitrogen adsorption.

EXPERIMENTAL

Materials

The materials used were Mallinckrodt's Acid Silicic S. L. (standard luminescent) and Mallinckrodt's Acid Silicic Special Bulky. The laboratory designations were A–33 and A–41, respectively. Both materials are precipitated silica gels of high purity, with the following specifications: heavy metals (as lead), 0.0005% max.; alkali salts (as sulphates), 0.10% max.; sulphate, 0.01% max.; chloride, 0.01% max.; and iron, 0.001% max. Partly because the silica samples were better than 99.9% pure (except for water), and partly because both types of silica contained about the same kinds and amounts of impurities, the heats of solution were not corrected for impurities.

Preparation of Batches

Preliminary drying was done by evacuating at 25°C. until the water vapor pressure of the hydrous silica was equal to that of ice at −78°C. (0.5 μ of mercury). The apparatus used was described by Copeland and Hayes (7). The batches thus obtained were designated A–33–1 and A–41–1. Samples with lower water contents were prepared by vacuum drying at higher temperatures. A two-stage mercury diffusion pump was used, backed by a Welch "Duoseal" pump. The pressure was less than 10^{-6} mm. of mercury. The temperature was raised very slowly to avoid blowing the finely divided material into the vacuum line. The drying schedules are shown in Table I.

Preparation of Samples

After the batch was prepared, it was transferred under vacuum into a controlled-atmosphere cabinet. Air was forced into the cabinet so as to maintain a slightly higher than atmospheric pressure. The air was first passed through four drying towers: one containing soda lime, the three others anhydrone (anhydrous magnesium perchlorate). Air was then admitted to the evacuated tube containing the batch; and the batch was quickly distributed

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TABLE I

DRYING SCHEDULES OF SILICA BATCHES

Batch designation	Drying temperature, °C.	Heating time to reach drying temperature, hr.	Drying temperature maintained, hr.
A–33–1	25	—	—
A–33–13	150	28	76
A–33–10	180	31	88
A–33–12	205	28	64
A–33–2	210	8	64
A–41–1	25	—	—
A–41–2	180	27	40
A–41–3	240	6	72

among four weighing bottles. The silica in each bottle was divided in the following manner: first, a 0.5 gm. sample was taken for ignition loss, then three samples (0.7, 1.0, and 1.3 gm.) for the calorimetric work, than a 1.0 gm. sample for surface area measurement or X-ray diffraction, and finally a 0.5 gm. sample for ignition loss. (The weights are approximate.) The container of each sample was covered, and each crucible and weighing bottle was placed in a separate weighing bottle. The cover of the outer weighing bottle was grease-sealed. The 24 samples were kept in ascarite–anhydrone desiccators until used. Immediately before use, each sample was taken out of the outer container and weighed in the inner container without removing its cover.

The samples were exposed to the atmosphere only while they were being dropped into the calorimeter, which period averaged 15 sec. for the A–33 and 27 sec. for the A–41 samples. Experiments, similar to those described in an earlier paper (4), were performed to ascertain the amount of moisture picked up during this time. The average pickup was 0.2 mgm./gm. of silica; thus, the error introduced by this factor was found negligible.

Measurements

1. The heats of solution were determined by a calorimeter that was a modification of the one used by Verbeck and Foster (19). The changes, as well as the experimental procedure, were described before (5). The acid mixture used was 8 ml. of 49.4% hydrofluoric acid with sufficient 2 *N* nitric acid added to make the total weight 420 gm. Each sample dissolved in less than three minutes. The solutions appeared to be clear for the 0.7 and 1.0 gm. samples, and slightly cloudy for the 1.3 gm. samples.

2. The specific surface areas of the eight batches of silica were determined by the B.E.T. method (3) using nitrogen at liquid nitrogen temperature as the adsorbate. Samples of the three A–41 batches showed a rather unusual behavior. As the sample was sealed to the adsorption line, a small amount of water condensed on the inner wall of the sample tube. The sample was then evacuated for several hours at 10^{-6} mm. of mercury pressure, nevertheless the nitrogen surface area measured was only about one-third of its expected value. The equilibration was very slow. Evacuation for 16 hr. at 10^{-6} mm. pressure increased the speed of equilibration and raised the surface area to

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about two-thirds of its expected value. Gentle heating with a small, smoky gas flame for about three minutes presumably removed all the adsorbed water, because thereafter the equilibration was fast and the surface area rose to its expected value. No such difficulty was encountered with samples of the A–33 batches. Shorter or longer evacuation, heating or no heating, resulted in quick equilibration and the same nitrogen surface area.

3. The specific surface areas of two batches of silica, A–33–1 and A–41–1, were determined also by water vapor adsorption, using a gravimetric method. Four relative pressures were used, produced in vacuum desiccators at 23.8°C. by means of saturated solutions of $NaOH \cdot H_2O$, $LiCl \cdot H_2O$, $KC_2H_3O_2 \cdot 1.5H_2O$, and $MgCl_2 \cdot 6H_2O$. The relative pressures of these hydrates at 25°C. are 0.0703, 0.1105, 0.2245, and 0.3300, respectively (18). Even though the relative humidities of the hydrates change with temperature (21), the changes are so slight that they do not affect the B.E.T plots; consequently, in the calculations the 25°C. values were used. A sample of each silica, in a small Erlenmeyer flask, was placed in each desiccator; the desiccators were then evacuated, and allowed to stand in a constant temperature room at 23.8±0.6°C. Periodic weighings showed that equilibrium was attained in less than two weeks.

4. Density determinations were made by water displacement in Welds type pycnometers. X-ray diffraction patterns were obtained by means of the equipment described before (2). Ignitions were carried out in platinum crucibles in a muffle furnace at 1050°C.

RESULTS

The heats of solution of the five batches of the A–33 and of the three batches of the A–41 series at different stages of dehydration and at different weights are given in Table II. The weights in the table are not the actual sample weights but the weights of silica in the samples; the heats of solution are, likewise, reported per gm. of silica, rather than per gm. of sample. The heats of solution were different at different weights, indicating relatively large concentration effects.

The specific surface areas obtained by nitrogen adsorption are shown in in Table III. The molecular area of nitrogen was assumed to be 16.2 Å^2 (4). The average values of the surface areas were 701.1, 709.7, 714.2, 666.2, and 665.9 meters^2/gm. of silica for A–33–1, A–33–13, A–33–10, A–33–12, and A–33–2, respectively; the A–41 samples had almost identical surface areas, with an average of 382.1 meters^2/gm.

The ignition losses of the eight sets of samples are also shown in Table III. Since analyses performed on several samples indicated no carbon dioxide, the entire ignition loss was attributed to water. The average values of the ignition losses were 0.0686, 0.0631, 0.0569, 0.0515, and 0.470 gm./gm. of silica for A–33–1, A–33–13, A–33–10, A–33–12, and A–33–2, respectively; and 0.0500, 0.0471, and 0.0428 gm./gm. of silica for A–41–1, A–41–2, and A–41–3, respectively.

The total water contents of silica batches A–33–1 and A–41–1 at four relative pressures are shown in Table IV.

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TABLE II

HEATS OF SOLUTION OF MALLINCKRODT'S S. L. GRADE SILICA AND SPECIAL BULKY SILICA

Sample	Weight, gm. of silica	Heat of solution, cal./gm. of silica
S.L. grade silica		
A–33–1	0.6815	605.91
	0.7004	607.07
	0.7006	607.20
	0.9261	604.52
	0.9557	603.28
	1.0063	602.80
	1.2250	600.73
	1.2485	600.18
A–33–2	0.6638	609.09
	0.6654	610.20
	0.6915	608.86
	0.9484	608.72
	0.9526	608.66
	0.9542	606.47
	0.9948	606.57
	1.2349	604.77
	1.2384	606.77
A–33–10	0.6541	608.63
	0.6574	608.85
	0.6755	611.45
	0.6809	612.16
	0.9592	607.41
	0.9735	606.79
	0.9791	608.51
	0.9843	607.96
	1.2282	606.24
	1.2625	604.99
	1.3010	603.35
A–33–12	0.6589	609.86
	0.6689	607.94
	0.7399	608.31
	0.9417	607.82
	0.9720	603.99
	0.9818	606.26
	1.2433	603.15
	1.3023	604.17
	1.3192	602.45
A–33–13	0.6662	609.35
	0.6738	608.38
	0.6823	608.37
	0.6836	607.22
	0.6976	607.23
	0.9484	606.57
	0.9506	606.43
	0.9536	607.42
	0.9771	605.57
	0.9790	605.79
	1.2302	604.34
	1.2321	603.34
	1.2517	602.65

Sample	Weight, gm. of silica	Heat of solution, cal./gm. of silica
Special Bulky silica		
A–41–1	0.5975	590.49
	0.6227	591.05
	0.7227	593.30
	0.7423	588.76
	0.9043	590.57
	0.9261	593.75
	0.9559	590.39
	0.9699	587.18
	1.2181	585.46
	1.2200	588.13
	1.2449	587.63
	1.2563	587.96
A–41–2	0.6493	594.90
	0.6625	595.19
	0.6725	591.07
	0.7438	592.43
	0.9158	590.25
	0.9603	589.92
	0.9648	588.25
	1.0054	591.07
	1.2396	588.17
	1.2488	587.85
	1.2522	585.71
	1.2951	588.46
A–41–3	0.6748	593.93
	0.6930	595.88
	0.7310	591.07
	0.9515	590.84
	0.9572	592.85
	0.9929	592.72
	1.0232	589.22
	1.2540	586.98
	1.2881	585.43
	1.3044	588.25

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TABLE III

SPECIFIC SURFACE AREAS AND IGNITION LOSSES

Sample	Area, m.²/gm. of silica	Ignition loss, gm./gm. of silica
A–33–1	694.3, 701.6, 707.4	0.0682, 0.0686, 0.0687, 0.0688
A–33–2	654.3, 677.5	0.0452, 0.0471, 0.0471, 0.0486
A–33–10	709.5, 714.0, 719.2	0.0560, 0.0562, 0.0566, 0.0567, 0.0574, 0.0577, 0.0580
A–33–12	664.5, 667.9	0.0505, 0.0506, 0.0512, 0.0517, 0.0523, 0.0526
A–33–13	709.1, 709.6, 710.5	0.0616, 0.0619, 0.0620, 0.0621, 0.0622, 0.0630, 0.0632, 0.0633, 0.0634, 0.0637, 0.0640, 0.0640, 0.0640, 0.0647
A–41–1	382.5	0.0489, 0.0497, 0.0499, 0.0500, 0.0500, 0.0502, 0.0502, 0.0511
A–41–2	381.6	0.0461, 0.0465, 0.0466, 0.0474, 0.0476, 0.0486
A–41–3	382.3	0.0417, 0.0421, 0.0430, 0.0430, 0.0432, 0.0438

TABLE IV

VARIATION OF TOTAL WATER CONTENT WITH RELATIVE PRESSURE AT 23.8°C.

Relative pressure	Total water content, gm./gm. of silica	
	A–33–1	A–41–1
0.0703	0.1352	0.1074
0.1105	0.1601	0.1212
0.2245	0.2159	0.1479
0.3300	0.2558	0.1633

DISCUSSION

Analysis of Data

If all A–33 samples had identical body structures, it follows that for any sample dissolved in the calorimeter

[1] $$H_{ijk}+w_j h-A_j \epsilon_s = H_k,$$

where H_{ijk} is the heat of solution in cal./gm. of silica of the ith sample of the jth batch, having weight k;

w_j is the average bound water content of the jth batch in gm./gm. of silica;

h is the average heat of hydration of the oxide surface (siloxane) to the hydroxylic surface (silanol) (12) in cal./gm. of water;

A_j is the average specific surface area of the jth batch in meters²/gm. of silica;

ϵ_s is the average surface energy (or surface enthalpy) of the siloxane surface in cal./meters²;

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and H_k is the heat of solution in cal./gm. of silica of a sample of weight k with zero bound water content and zero surface.

A least squares analysis of the data was made by the method of Deming (8). This method enables one to take into account the errors in all measured quantities. Dr. Paul Seligmann of this laboratory derived the equations for the evaluation of the weighted means and standard errors of h, ϵ_s, $H_{0.7}$, $H_{1.0}$, and $H_{1.3}$. The derivation required considerable statistical skill, and the evaluations involved hundreds of operations. The results are shown in Table V, Columns 2 and 3.

TABLE V

RESULTS OF LEAST SQUARES ANALYSIS

	A–33 data alone (5 sets)		A–33 and A–41 data (8 sets)	
	Weighted mean	Standard error	Weighted mean	Standard error
$H_{0.7}$ (cal./gm. of silica)	580.6	1.6	580.2	0.5
$H_{1.0}$ (cal./gm. of silica)	578.1	1.6	578.0	0.5
$H_{1.3}$ (cal./gm. of silica)	575.3	1.6	575.3	0.5
h (cal./gm. of water)	278.3	7.6	258.6	13.0
ϵ_s (cal./meters^2)	0.0634	0.0027	0.0618	0.0007

If it is assumed that the A–41 batches had the same body structures as the A–33 batches (in other words, if the A–41 batches differed from the A–33 batches *only* in bound water content and specific surface area), the three sets of data obtained for A–41 can be combined with the five sets of data obtained for A–33, and the five parameters can be evaluated from the eight sets of data with the help of Dr. Seligmann's equations. The results are shown in Table V, Columns 4 and 5.

1. Comparison of the zero bound water and zero surface heat values in Columns 2 and 4 shows that least squares analysis of the five sets of data obtained for the A–33 samples alone gave results that were practically identical with those obtained from analysis of all eight sets of data. (The A–41 data could not be analyzed alone in a similar manner because all samples had the same specific surface areas.) The close similarities between the five-set and the eight-set heats of solution indicate strongly that the body structures of A–33 and A–41 were practically identical.

2. Because the body structures of A–33 and A–41 were found to be practically identical, it is a legitimate procedure to evaluate ϵ_s and h from the combined data obtained for all eight batches. That a more accurate value can be obtained for ϵ_s by such a combination is clear from the following considerations. The difference between the specific surface areas of the high and low surface A–33 batches was about 40 meters^2/gm. but the difference between the specific surface areas of the A–33 and A–41 batches was about 300 meters^2/gm. Since the error in the surface area determination is about the same for each batch, the error in the differences between surface areas is much smaller on a percentage basis for the eight-set data than for the five-set data. Table V

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shows that the standard error of ϵ_s is four times as large for the latter as for the former. This indicates that the eight-set values give better estimates of the parameters than the five-set values.

The eight-set value of ϵ_s in Table V is 0.0618 cal./meter^2, with a standard error of ± 0.0007 cal./meter^2. Thus, *the surface energy of amorphous silica of zero water content—or the energy of the pure siloxane surface—at 23°C. is 259±3 ergs/cm.*^{2} This is an average surface energy, and the surface may possess some sites of higher and lower energy than the average. There was some indication, however, that the silica surfaces were more uniform than those ordinarily encountered in adsorbents. The B.E.T. plots of adsorption isotherms usually deviate from linearity below a relative pressure of 0.05, which is attributed to adsorption on high energy sites at low pressures. The B.E.T. plots of the nitrogen adsorption isotherms for A–33 and A–41 remained linear down to the lowest relative pressures measured in these experiments, about 0.005. Perhaps such uniformity of surface is less surprising in an amorphous substance than it would be in a crystalline adsorbent, since different exposed crystal faces, as well as edges and corners, are bound to introduce heterogeneity.

The surface energy of 259 ergs/cm.^{2} is based on the assumption that the molecular area of nitrogen is 16.2 Å^2. If Livingston's (15) value of 15.4 Å^2 were used, the surface energy would be 5% larger. The standard error of ±3 ergs/cm.^{2} does not include the uncertainty in the molecular area of nitrogen.

As stated in the introduction, the surface energy of vitreous silica, estimated by Iler and Yates (11) from the data of Shartsis and Spinner (17), was 275±25 ergs/cm.^{2} This value agrees with that reported here within 16 ergs/cm.^{2}

3. The eight-set value of h in Table V is 258.6 cal./gm. of water, with a standard error of ±13.0 cal./gm. Thus, *the heat of hydration by liquid water of the siloxane surface to silanol surface, or the heat of chemisorption of liquid water on the siloxane surface, at 23°C. is 4660±230 cal./mole of water.* This is an average heat of hydration; but, as pointed out before, the siloxane surface was probably rather uniform.

4. The energy of the silanol surface can be calculated from ϵ_s and h, provided the area occupied by a water molecule on the surface is known. Iler (13) showed that the area to be assigned to an SiOH group on the surface of amorphous silica of specific gravity 2.20 is close to 12.5 Å^2. Since the chemisorption of a water molecule results in two SiOH groups (12), the area assignable to a water molecule is 25.0 Å^2. On the basis of this area, the heat of hydration of the siloxane surface to silanol at 23°C. amounts to 130±7 ergs/cm.^{2} and *the average surface energy of hydrous amorphous silica with a completely hydrated surface—or the energy of the pure silanol surface—at 23°C. is 129±8 ergs/cm.*^{2} The standard error does not include the uncertainty in the molecular area of water.

It is worth noting that the total energy of the silanol surface is only slightly higher than the total surface energy of liquid water, which is 118.5 ergs/cm.^{2} at 25°C. (10). This was predicted by Iler (11). Hydrous silica and liquid water are amorphous substances, and the chemical compositions of their surfaces

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should show considerable similarities if, as the presently accepted model postulates, the hydroxyl groups in the silanol surface are on top, and the silicon atoms are below the hydroxyl groups (13). The present results support this model. If the silicon atoms were on top, or even on the same level with the hydroxyl groups, it would be difficult to understand the close similarity between the surface energies of water and hydrous silica.

The total energy of the hydrated surface of amorphous silica is probably lower than that of most solids. The surface free energy is bound to be even lower. Thus, the tendency to pass from smaller to larger particles is relatively small, which may explain many of the unusual colloidal properties of hydrous amorphous silica (11).

Another fact worth noting is that the difference between the energies of the siloxane and the silanol surface, 130 ergs/cm.^{2}, is the same as the difference between the surface energies of calcium oxide and calcium hydroxide, reported in an earlier paper (4). This may be just a coincidence, but there seems to be at least an indication here that the hydration of the surface involves a conversion of the surface oxide ions into surface hydroxyl ions both in calcium oxide and in silica and, further, that both in calcium oxide and in silica, the oxide ions are on top and the positive ions below. Thus, the facts noted in this and the previous paragraph tend to confirm Weyl's hypothesis (22) as to the structures of ionic surfaces.

Identity of Body Structures

1. The differences between the heats of solution of A–33 and A–41 samples could be ascribed to differences between surface properties (surface water content, specific surface area) only if the body structures of A–33 and A–41 were identical. In an earlier paper (4), strong evidence was cited for the identities of the body structures of high and low surface calcium oxide and calcium hydroxide on the basis of X-ray diffraction measurements (precision determination of lattice parameters, line broadening). It was impossible to do this for the silica samples, because the diffraction pattern of each sample consisted of a single very wide band only, with a broad maximum at d = 3.95 Å. The samples also showed pronounced low angle scattering. A radial distribution analysis, such as that carried out by Warren (20), could have supplied useful indications as to the identity of the body structures of A–33 and A–41, but the appropriate equipment was not available.

2. In order to show some independent evidence regarding the body structures, density measurements were performed on several batches of A–33 and A–41. It soon appeared that a thorough investigation of the density would be a research problem comparable in extent to that described in this paper. Because of this, only some tentative results can be reported here.

If the density is plotted against the fraction of the surface covered with bound water, and the data are extrapolated to zero surface covering, the density values obtained are

$$d_{A-33} = 2.28 \pm 0.01 \text{ gm./cc. and } d_{A-41} = 2.29 \pm 0.01 \text{ gm./cc.}$$

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at 26°C. If the density of packing of the silicon atoms in the surface is slightly lower than that in the body, d_{A-41} should be somewhat larger than d_{A-33}, since A–33 has a much larger specific surface area than A–41.

3. The decisive evidence regarding the identity of the body structures of A–33 and A–41 was found in the zero bound water and zero surface heats of solution shown in Table V for the five-set data and the eight-set data. The significance of the close agreement between the heat values will be more apparent after the following considerations. The density difference between A–33 and A–41 is not significant statistically; nevertheless, the 0.44% difference between the densities may be real. If the energy content per gm. of the body of amorphous silica is inversely proportional to r^3, where r is the average distance between silicon atoms, a 0.44% change in density would cause a change of 2.5 cal./gm. of silica in the heat of solution. The average difference between the five-set and eight-set heat values in Table V is less than 0.2 cal./gm. of silica. Thus, the close agreement between the heat values indicates close similarity between the body structures. If the density difference between A–33 and A–41 is real, it is caused by a difference between the densities of packing of atoms in the surface and in the body, as was pointed out in the previous section.

Bound Water Content

1. The value of h, 258.6 cal./gm. of water, represents the heat of hydration of the siloxane surface correctly only if there was no physically adsorbed water in the A–33 and A–41 samples. If one takes Iler's value of 25 Å^2 for the molecular area of bound water, the nitrogen surface area of A–33 indicates that the amount of bound water at complete coverage would be 0.084 gm./gm. of silica. Greenberg (9) determined the amount of bound water in Mallinckrodt's S. L. grade silica at complete coverage of the surface in three different ways and obtained the values 0.090, 0.083, and 0.079 gm./gm. of silica. A–33–1, equilibrated at 25°C. and a vapor pressure of 0.5 μ of mercury, contained 0.0686 gm. of water of silica, and all other batches of A–33 contained less water. It seems, therefore, that the A–33 samples contained only bound water, and the surfaces of the samples were only partly covered with bound water.

2. It is more difficult to show the same for A–41. Greenberg's values for the bound water content of Mallinckrodt's Special Bulky silica, determined in three different ways, were 0.071, 0.066, and 0.049 gm./gm. of silica; but the nitrogen surface area of A–41 combined with Iler's molecular area for water indicates only 0.046 gm. of bound water per gm. of silica at complete coverage. The water values for A–41–1, A–41–2, and A–41–3 were 0.0500, 0.0471, and 0.0428 gm./gm. of silica, respectively; which would correspond to 109.3, 103.0, and 93.6% coverage.

These results can be explained by assuming that the excess water in A–41–1 and A–41–2 was physically adsorbed water and not bound water. This hypothesis was tested by using the $H_{0.7}$, $H_{1.0}$, $H_{1.3}$, and ϵ_s values of Table V, and calculating h for each of the three batches of A–41 from the experimental

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results. The value of h was found to be almost exactly the same for all three batches. This means either that all three batches contained only bound water, or that the average heat of adsorption of water physically adsorbed on the *most active* fraction of the silanol surface was approximately equal to the average heat of hydration of the *entire* siloxane surface. Both alternatives are reasonable, and no decisive evidence exists at present that would enable one to make a clean-cut choice.

The second alternative is favored by the present investigators, because the first one is out of line with the accepted views on the mechanism of hydration of the siloxane surface. The average area per silicon atom on the surface of amorphous silica is 12.5 Å^2, and it is generally accepted that a water molecule produces two surface SiOH groups. However, if all the water in batch A–41–1 was bound water, the molecular area of chemisorbed water was not 25 Å^2, but 22.9 Å^2. This would mean that there were more hydroxyl groups on the surface than Si atoms.

Of course, the above argument is not decisive; it is possible that the area to be assigned to a water molecule was 22.9 Å^2. In that case, ϵ_s and h in Table V would remain unaffected, but the surface energy of the fully hydrated surface would become 117 ergs/cm.^{2}, instead of 129 ergs/cm.^{2}

3. If it is assumed that the ultimate silica particles are equal spheres, the nitrogen surface areas of A–33 and A–41 correspond to particle diameters of about 37 and 64 Å, respectively. Batches A–33–1 and A–41–1 were dried to a near-equilibrium state at 25°C. and a water vapor pressure of 5×10^{-4} mm. of mercury. It is interesting to note that at this vapor pressure the surface hydrate was perfectly stable on the larger particles; the surface of A–41–1 was completely covered with bound water. On the other hand, the surface hydrate on the smaller particles partly decomposed; the surface of A–33–1 was only about 80% covered with bound water. These examples illustrate the effect of particle dimension or the curvature of the surface on the stability of the surface film. The effect of size or curvature upon the stability of the silica particles themselves is illustrated by the fact that A–33 began to sinter at 200°C., whereas A–41 showed no sintering at 300°C.

Physical Adsorption of Water

The determination of the specific surface areas of A–33–1 and A–41–1 by the B.E.T. method using water vapor at 23.8°C. as the adsorbate encountered two difficulties: (*a*) distinguishing between bound water and physically adsorbed water, and (*b*) uncertainty in the molecular area of physically adsorbed water.

1. The energy of interaction between a polar molecule and an ionic surface is much greater than that between a nonpolar molecule and an ionic surface. For example, Chessick, Zettlemoyer, Healey, and Young (6) showed that the net heat of physical adsorption of an alcohol on a rutile (TiO_2) surface was 361 ergs/cm.^{2}, whereas that of a hydrocarbon was 92 ergs/cm.^{2} The difference was almost entirely due to the energy of interaction between the dipole of the adsorbate and the electrostatic field of the surface. Because of the high energy

of interaction between water and an ionic surface, it is difficult to make a clean-cut separation between physically and chemically adsorbed water.

2. The structure of the underlying surface has little effect on the packing of physically adsorbed nitrogen; consequently, it is possible to assign a single value to the molecular area of nitrogen that is valid, to a good approximation, for any adsorbent. This is not true of physically adsorbed water. The ions of the adsorbent surface orient the dipole of the water molecule, and the packing of the adsorbed molecules is influenced by the structure of the underlying surface. An example of this is found in some experiments of Jura (14), who determined the specific surface areas of five ionic adsorbents by means of the B.E.T. method, using nitrogen and water vapor as adsorbates. If it is assumed that the molecular area of nitrogen was the same on all five adsorbents, then the molecular area of water varied over a range of 35%, from the highest to the lowest value.

It is especially interesting to note the results for quartz among Jura's five adsorbents. On the basis of the customary 16.2 Å^2 for the molecular area of nitrogen, the molecular area of physically adsorbed water on the quartz surface was 11.3 Å^2. If the average distance between silicon atoms on the surface of quartz is the same as in the body of the crystal, the average area assignable to a silicon atom on the quartz surface is 11.24 Å^2. This indicates that the number of silicon atoms on the surface determines the packing of physically adsorbed water molecules. If the same is true for amorphous silica, the molecular area of physically adsorbed water molecules on the surfaces of A–33 and A–41 was 12.5 Å^2.

3. The total water isotherms of A–33–1 and A–41–1 at 23.8°C. were determined in the relative pressure range 0.07 to 0.33. The results were shown in Table IV. If one assumes a certain value for bound water, and further assumes that the bound water content did not vary in the relative pressure range investigated, subtracting the assumed value from the total water gives the amount of physically adsorbed water. A B.E.T. plot of the physical adsorption isotherm, combined with a molecular area of 12.5 Å^2, then gives the specific surface area of the adsorbent. The variation of the specific surface area with assumed bound water content is shown in Fig. 1.

The bound water content of A–33–1 was 0.0686 gm./gm. of silica at the beginning of the experiment. If no hydration of the surface occurred in the course of the experiment, the surface area measured by water adsorption was 658 meters^2/gm., as Fig. 1 shows. Iler stated that the siloxane surface "hydrates scarcely at all at a relative humidity of, say, 40 or 50%."The maximum relative humidity used in these experiments was 33%, and the results confirm Iler's statement. The surface area of 658 meters^2/gm. is 6% smaller than the value obtained by nitrogen adsorption. Any appreciable hydration of the surface in the course of the adsorption experiments would make the discrepancy greater.

The water content of A–41–1 was 0.0500 gm./gm. of silica at the start, but it is possible that a part of this was adsorbed water, as discussed before. The nitrogen area indicated a bound water content of 0.0460 gm./gm. of

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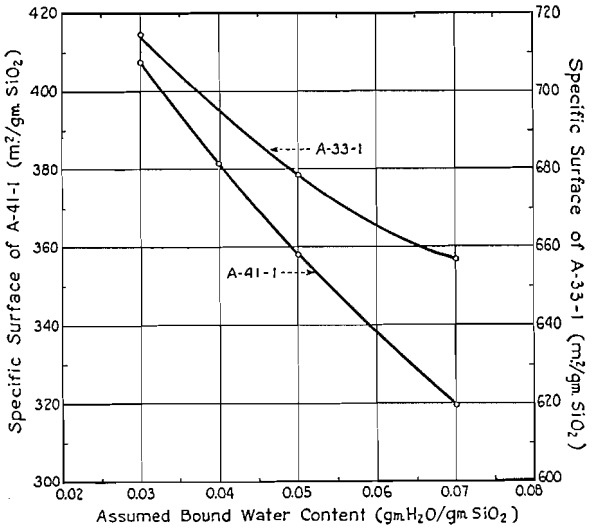

FIG. 1. Variation of specific surface area with assumed bound water content.

SiO_2 at complete coverage. According to Fig. 1, the values of 0.0460 and 0.0500 gm. of water per gm. of silica correspond to surface areas of 367.5 and 358.5 meters²/gm. respectively. The former is 4%, the latter 6%, smaller than the nitrogen adsorption area.

Thus, the surface areas obtained by water vapor adsorption were about 4 to 6% smaller than the nitrogen areas. It is possible that 16.2 Å² is too large for the molecular area of nitrogen. Livingston (15) favors the value of 15.4 Å², which is 5% smaller than the one used here. It is also possible that 12.5 Å² is too small for the molecular area of water. Livingston calculated the molecular area of water from the two-dimensional van der Waals constant *b*, and obtained 13.1 Å², which is 5% larger than the value used here. Obviously, it is also possible that the molecular area of nitrogen was somewhat too large and the water area somewhat too small, the two errors adding up to about 5%. Adequate data are lacking between these alternatives, but the good agreement between the surface area values obtained by nitrogen and water adsorption is gratifying.

The value of the *c* constant (3) of the B.E.T. equation was 9 for A–33–1 and 23 for A–41–1, indicating a stronger binding of physically adsorbed water to the surface of the latter. Since the surface of A–41–1 was a pure silanol surface, whereas the surface of A–33–1 was a mixed silanol–siloxane surface, the implication is that the heat of adsorption of water on the silanol surface is greater than on the siloxane surface. This is in agreement with certain experiments reported by Iler (12), indicating that the siloxane surface is somewhat hydrophobic.

ACKNOWLEDGMENT

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A NOTE ON THE TEMPERATURE DEPENDENCE OF THE ELECTRICAL RESISTANCE OF SALT SOLUTIONS ADSORBED IN POROUS GLASS[1]

By Max Huber[2] and E. A. Flood

INTRODUCTION

It has been shown that the flow of liquids through "Vycor" glass is roughly inversely proportional to the liquid viscosity (5). The temperature variations of the specific electrical resistances of some dilute salt solutions, e.g. NaCl, follow quite closely the temperature variation of the viscosity of water (4, 6, 7). If such solutions are adsorbed as a whole without causing marked concentration gradients, specific resistances of the adsorbed solutions should give rough measures of adsorbate mobilities and the temperature coefficients of these resistances should afford some measure of the "viscosity" activation energies.

Accordingly we have carried out some exploratory measurements of the specific electrical resistances, at various temperatures, of 0.1 *N* solutions of NaCl and of KCl when contained (adsorbed) within the micropore system of Vycor glass.

Our results indicate little "selective" adsorption of these salts.

The true specific resistances of the solutions depend on the pore structures. Assuming a pore structure consisting of three mutually perpendicular non-intersecting straight uniform capillaries, the specific resistances of the solutions were found to be about three times that of the bulk solutions. This is consistent with a pore structure consisting of relatively large islands interconnected by narrow necks. This latter structure is consistent with the method of manufacture of these porous glasses (5).

The temperature coefficients of the specific resistances of the NaCl and KCl solutions are somewhat greater than those of the bulk solutions.

It is concluded that the viscosities of adsorbed 0.1 *N* NaCl and 0.1 *N* KCl solutions are of the same order as those of the bulk solutions.

This work is part of a general investigation concerning the flow of adsorbed fluids. We have described the flow of adsorbed gases through the micropore systems of activated carbons as a laminar viscous flow of liquid films of adsorbate (2). It has been shown that the temperature coefficient of the viscosity of adsorbed water is somewhat greater than that of water in bulk. This has been attributed to surface forces and is consistent with a surface potential of the order of 2–5 kcal. per mole adsorbed (3). This order of surface potential is consistent with the temperature coefficients of the resistances reported below.

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EXPERIMENTAL

1. Materials

Porous glass (Vycor No. 7930) tubes were obtained from the Corning Glass Works. It was stated that the Vycor had the following properties:

Apparent density	1.45
Void space per cc.	0.34
Average pore diameter	40 Å
Surface area B.E.T. N_2	120 meters^2/gm.
NH_3	204 meters^2/gm.

The KCl and NaCl used were Merck's reagent grade.

The conductance of the distilled water used in the experiments and for the making of the solutions varied from about 2 to 5×10^{-6} Ω^{-1}.

2. Electrical Apparatus and Procedures

Fig. 1 illustrates the apparatus used for measurement of the resistance of the walls of the Vycor test tubes, the micropores of which contained the solutions. Alternating current was supplied from a Hewlett and Packard (Model 205 AG) 1000 c.p.s. 15 w. generator, impedance adjustable between 50 and 5000 Ω. The voltage drops across the porous glass and a standard resistance box (Leeds and Northrup 4749) were measured by means of a Hewlett and Packard Decibel-Voltmeter (Model 400 c). The precision of readings was of the order of 1%. The measurements were always reproducible within the precision of instruments.

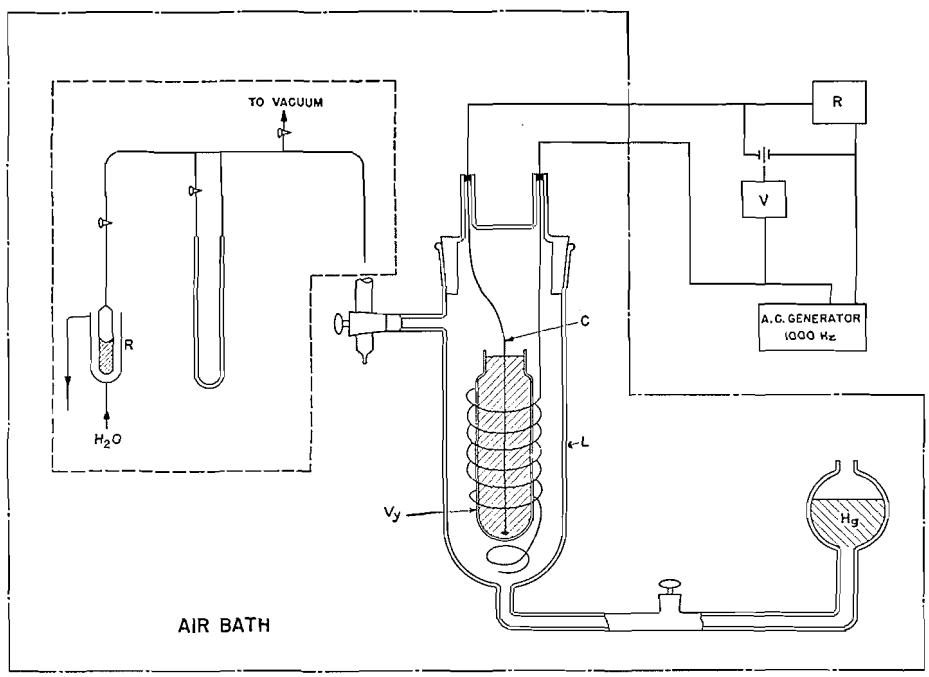

FIG. 1.

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The Vycor tubes, *Vy* (Fig. 1), were test-tube shaped but with somewhat restricted necks. The necks were fired and practically non-porous.

A test tube after immersion for 8–10 days in the appropriate solution was wiped once with adsorbent paper (Kleenex) to remove excess liquid, placed in the copper helix holder, filled with mercury, and quickly placed in the tube *L*. The Vycor tube (*Vy*) was held in place in the outer tube *L* by means of the stout copper wires (*C*) which also served as electrical leads. Mercury was then allowed to rise from the reservoir (*Hg*) until above the Vycor tube after which it was lowered to 2 mm. below the edge of the Vycor tube. The tube was then evacuated and opened to the water vapor system where any desired humidity could be maintained. The outer mercury level would be lowered during equilibrations at various relative humidities. In general, it was found that the resistance of the glass between the two volumes of mercury was independent of the mercury pressure, the resistance being the same in vacuum and at 760 mm.

Two distinctly different types of measurement were made: (*a*) resistances of the salt solutions contained in the micropore system between the two volumes of mercury where the temperature of the mercury and salt solution was varied and (*b*) resistances at 35.3°C. of salt and water contained in the micropore system where the water content varied as the water equilibrium pressure was varied. Resistances at various temperatures showed little or no drift with time. Usually within five minutes after raising or lowering the temperature, the resistances became constant within the experimetal error.

RESULTS

Preliminary experiments with fragments of one of these Vycor tubes indicated the following:

When dried at 130°C. for 15 hr. the weights were readily reproducible within 1%.

Water adsorption isotherms were essentially similar to those reported in the literature (1) and by the manufacturers although the quantity taken up at saturation varied from 0.22 to 0.24 gm. per gm. saturation which is somewhat less than usually found, namely 0.25 gm. per gm.

When red and blue litmus papers were laid on the wet Vycor tube no change in color could be detected after 15 min. However, when the tubes were immersed in 10% NaCl and similarly tested a faint acid reaction could be detected.

The specific resistance of the Vycor tubes as supplied when saturated with water was of the order of $1.5\times10^4\ \Omega$ while after continued washing and immersion in distilled water the resistance was of the order of $8\times10^4\ \Omega$. Evidently, the Vycor contains traces of electrolyte difficult to remove.

When Vycor fragments were immersed in salt solutions for 8 to 10 days, removed, wiped, and dried first in a desiccator and subsequently in vacuum at 130°C., the gains in weight corresponded closely to the filling of the void space with the salt solution in which they were immersed. For saturated KCl solutions the gains corresponded to slightly more than that corresponding

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to the saturated solution, while in the case of 10% NaCl solution the mean values corresponded to about 9% NaCl. Accordingly, it was judged that within the experimental error there was little or no selective adsorption and it is assumed that when the Vycor tubes are immersed in 0.1 N solutions of KCl and NaCl for 8 to 10 days the concentrations in the micropore system are close to 0.1 N.

The relation between the specific resistance of the solution within the micropore system and the measured resistance of the Vycor tube will depend upon the structure of micropore system as well as upon the dimensions of the tube. The mean wall thickness of the tubes (Nos. 1, 2, and 3) was between 0.12 and 0.13 cm. and the area of the porous part of the tube 37.0 cm. Accordingly, if ρ is the specific resistance of the solution, then the measured resistance, R, will be given by

$$R = \rho(0.125/37) \cdot F$$

where F is a factor depending on the micropore structure and the void volume, per cc. of glass, which we take as 0.34. If all of the pores are perpendicular to the axis of the tube and perfectly straight and uniform in cross section, $F = 1/0.34$. If only one-third of the pores are parallel with current, the remaining two-thirds not being interconnected and being perpendicular to the current direction, then $F = 3/0.34$. If the pores are intersecting, F will lie between these figures. If the micropore system is an interstitial type structure consisting of "islands" interconnected by necks, the factor can vary from something less than 3/0.34 to very large values, depending on the degree of isolation.

We have used the factor 3/0.34 in calculating specific resistances of the solutions, i.e., specific resistance = measured resistance × 34. In Fig. 2 the specific resistances of 0.1 N KCl solution (tube No. 3) and 0.1 N NaCl solution (tube No. 2) are plotted as functions of temperature. The I.C.T. values multiplied by suitable factors (KCl × 3.37, NaCl × 2.44) are plotted for comparison. A single point for 0.1 N KCl tube No. 1 is included. Evidently F is of the order of three, which suggests an interstitial structure where the "necks" are of the order of one-sixth of the diameters of the islands.

The measured resistances R, in ohms, of tube No. 1, which was immersed in 0.1 N KCl and then dried as above and equilibrated to various relative humidities, are presented in Table I.

TABLE I

ELECTRICAL RESISTANCE OF VYCOR TUBE NO. 1 (EXPOSED TO 0.1 N KCl) DURING ADSORPTION AND DESORPTION OF WATER (35.3°C.)

p/p_s	$R(\Omega)$	p/p_s	$R(\Omega)$	p/p_s	$R(\Omega)$
0.000	—	0.713	108	0.670	100
0.110	630,000	0.892	5.9	0.387	8670
0.388	9180	1.000	5.5	0.352	15,300
0.552	1150	0.756	21.7	0.000	1,500,000

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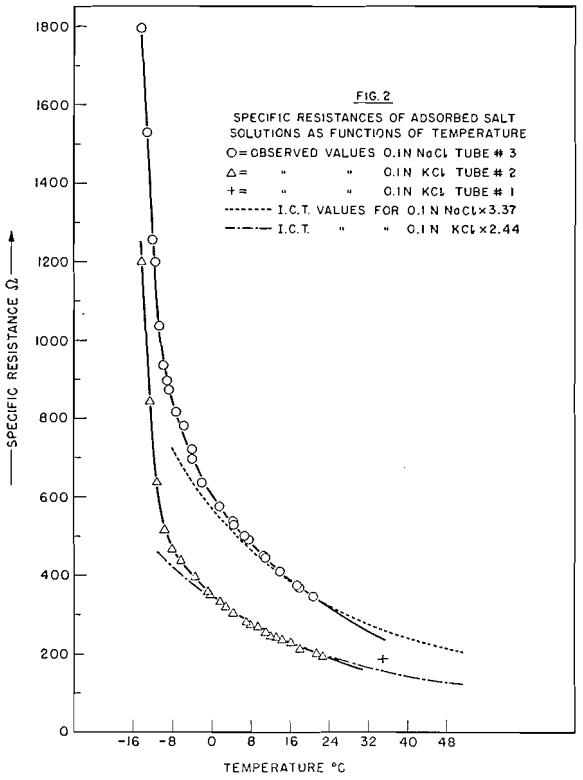

FIG. 2.

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THE PURITY OF SMALL SODIUM CHLORIDE PARTICLES PREPARED BY ELECTROSTATIC PRECIPITATION[1]

BY F. VAN ZEGGEREN,[2] H. P. SCHREIBER,[3] AND G. C. BENSON

Recently Benson and Benson (2) have attempted to determine the surface enthalpy of crystalline sodium chloride by measuring heats of solution of samples having different specific surface areas. The fine salt used in these

[1]*Issued as N.R.C. No. 4047.*
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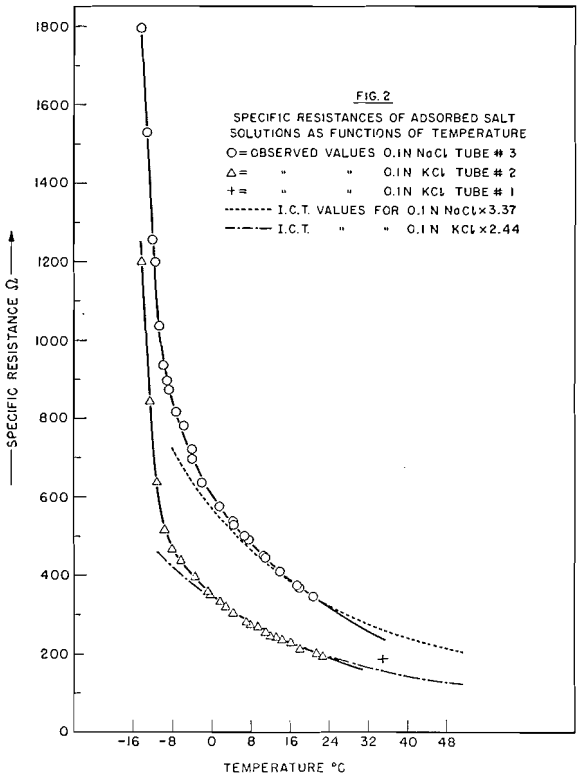

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experiments was made by electrostatic precipitation of a sodium chloride smoke. Essentially the same method of preparation has been employed by a number of other workers (6, 3, 11, 7).

In the course of the surface enthalpy study the following indications of impurities in the fine salt were noted:

(i) Some samples had a definite bluish hue and when dissolved in water gave alkaline solutions. Patterson, Morrison, and Thompson (7) have also reported obtaining a pH value as high as 9 under similar circumstances.

(ii) Other material which did not give any marked increase in pH nevertheless led to anomalous heats of solution. Thus finely divided salt, which had been thermally sintered to very small surface, apparently had a lower enthalpy than pure bulk crystals. Aqueous solutions of this material gave a positive diphenylbenzidine spot test (4) indicating the presence of nitrate or nitrite impurities.

The blue color and alkaline pH undoubtedly result from the presence of excess sodium in the fine material. The existence of blue salt in nature is well known (5) and recently Scott, Smith, and Thompson (8) have studied the absorption spectrum of salt which was colored blue artificially by a colloidal dispersion of sodium.

Since the occurrence of sodium nitrate impurity in fine sodium chloride prepared by electrostatic precipitation has not been considered by previous users of the method, the purpose of the present note is to give some indication of the extent of this contamination in salt samples prepared under various control conditions. This information should be of value in selecting operating conditions to minimize the content of this impurity.

EXPERIMENTAL

The apparatus used for the production of a sodium chloride smoke was essentially the same as that described by Thompson, Rose, and Morrison (10). A stream of carrier gas at room temperature and at a flow rate of 3.7 cu. ft./min. was obtained by heating liquefied gases. Three different nitrogen–oxygen mixtures were employed for this purpose. These were liquid air and liquid nitrogen produced in the Division of Pure Chemistry, N.R.C., and another grade of liquid nitrogen obtained from Linde Air Products Co., which contained approximately 18%, 2%, and 0.05% oxygen respectively.

The precipitator was a cylindrical Pyrex tube 40 cm. long and 6.5 cm. in diameter on the outside of which was wrapped a layer of brass shim. Alternating current voltages from 6 to 15 kv. (60 cycles/sec.) were applied between this layer and an axial 20 gauge platinum wire. The molten salt was maintained manually at an approximate temperature of 900° C. The temperature in the precipitator was about 40° C.

Samples of sodium chloride smoke were precipitated at various voltages using carrier gases of different oxygen content. X-ray diffraction examination confirmed the presence of sodium nitrate impurity in a number of these. The nitrate content of some of the samples was determined quantitatively by the ferrous sulphate titration method (9). In later work estimation of nitrate

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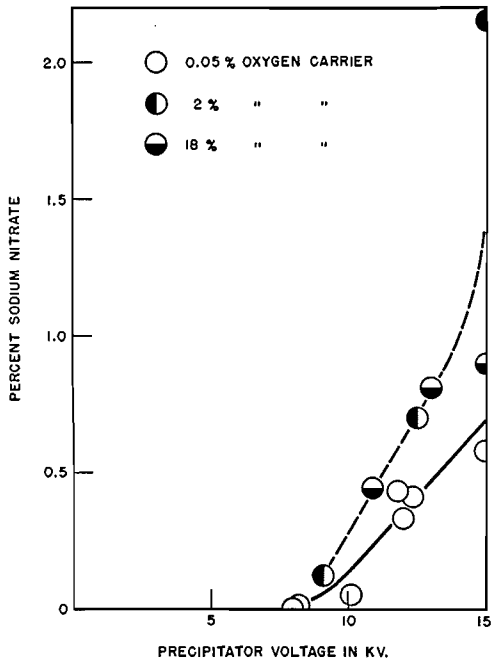

FIG. 1. Variation of nitrate content with precipitator voltage for different percentages of oxygen in the carrier gas.

based on the reaction with brucine (1) and using a photoelectric colorimeter was found to be more convenient.

Data derived from these analyses are illustrated in Fig. 1 where the per cent sodium nitrate content is plotted against the precipitator voltage for runs with the 18%, 2%, and 0.05% oxygen carrier gases. These results are only semiquantitative in nature since duplicate runs sometimes showed considerable variation in the nitrate content. In such cases an average value has been plotted in Fig. 1. It seems probable that this lack of reproducibility stems from variations in the detailed geometry of the discharge in the precipitator from run to run. Within the reproducibility of the experiments there is no significant difference between the results obtained with the 18% and 2% carrier gases and only one curve has been drawn through these data. The curve for the 0.05% case, however, is quite definitely lower. For both curves the nitrate content increases with precipitator voltage and in some cases the nitrate content may be as high as 1 to 2%.

Since samples prepared at high voltages usually showed traces of color as well, the possibility of a correlation between nitrate content and pH of an aqueous solution of the sample was examined. For this purpose the pH of 0.05 *N* solutions of some of the fine salt samples in boiled conductivity water was measured with a Beckman glass electrode meter. In plotting the results shown in Fig. 2 the pH of a similarly prepared 0.05 *N* solution of reagent grade sodium chloride has been adopted as a zero. Thus ΔpH is defined by

$$\Delta\text{pH} = \text{pH (fine salt solution)} - \text{pH (reagent salt solution)}.$$

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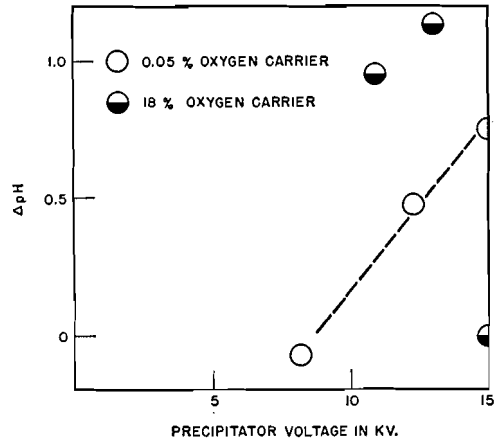

FIG. 2. Variation of ΔpH with precipitator voltage for different percentages of oxygen in the carrier gas.

For the 0.05% oxygen carrier ΔpH increases approximately linearly with precipitator voltage and hence in view of the data of Fig. 1, a fairly linear relation exists between ΔpH and nitrate content. However, when the oxygen content of the carrier is increased the use of pH alone as a criterion of purity becomes unsatisfactory. This is illustrated by the three points in Fig. 2 for the 18% oxygen carrier. In this case the ΔpH falls off at high voltages. The result plotted at 15 kv. is the average of +0.02, −0.08, and +0.03 obtained in three independent runs. Apparently when there is a high content of oxygen in the carrier gas the nitrate formation may be sufficient to annihilate the free sodium produced in the discharge process. Around 15 kv. and under the control conditions used in the present work this process reduces the ΔpH to zero. However this may not be the case at still higher voltages or under different control conditions. No attempt has been made to investigate this mechanism in detail since our primary interest is in the production of pure samples.

DISCUSSION

From the data presented in Figs. 1 and 2 it is evident that the precipitation voltage and oxygen content of the carrier gas should both be as low as possible. The minimum voltage at which any significant collection of salt can be obtained is 6 to 7 kv. and about 8 kv. gives a reasonable collection efficiency. Samples with areas 20–30 square meters/gm. have been prepared at this voltage under the present conditions of flow and temperature.* It is difficult to obtain large flow rates of very pure nitrogen and the 0.05% oxygen content gas used in the present work seems to be the best available under the present circumstances. If this is used as carrier with a precipitator voltage of 8 kv. the nitrate content should be less than 0.05%. As a further check several samples of salt prepared under these conditions were sintered thermally to have areas near zero and the heats of solution determined as in Reference 2.

By varying the flow rate up to 6 cu. ft./min. specific areas as high as 60 square meters/gm. have been obtained. Changes in flow rate do not appear to influence the purity of the product markedly.

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Without exception the enthalpies of the samples were greater than that of pure bulk salt and the differences, which were only a few calories/mole, could be accounted for by the remaining surface enthalpy of the sintered material which still had a small non-zero area.

A rough calculation shows that a nitrate content of about 0.3% would explain the intercept of −5.4 cal./mole reported in Reference 2. Since the carrier gas used in that work contained 2% oxygen and the operating voltage was about 10 kv. this estimate is quite in accord with the present findings.

The effect of this impurity on the surface enthalpy (i.e. the slope of the line in Reference 2) is difficult to estimate because of uncertainties in the energetics involved when a chloride ion is replaced by a nitrate ion and also because of lack of information about the distribution of nitrate ions in the lattice. In all probability the nitrate is formed at the surface of the particles while they are in the precipitator. If it is assumed that diffusion into the bulk of the crystal is relatively slow and that the particles are uniform cubes the percentage P of surface molecules which are sodium nitrate is given approximately by the formula

$$P = 1200(x/A)$$

where A is the area in square meters/gm. and x the weight per cent of sodium nitrate in the whole sample (x assumed small compared to 100%). Thus for material of area 30 square meters/gm. and containing 0.3% sodium nitrate, as high as 12% of the surface molecules might be sodium nitrate. In such a case some effect on the surface properties and in particular on the surface enthalpy is quite conceivable. However, any definite conclusion must await the results of the experimental redetermination of the surface enthalpy of sodium chloride now in progress.

ACKNOWLEDGMENTS

In conclusion, we wish to thank Mr. D. S. Russell of the Analytical Laboratory of the Division of Applied Chemistry, N.R.C., for performing the nitrate analyses by the ferrous sulphate method, and Dr. L. D. Calvert of the Metallurgical Chemistry Section of the Division of Applied Chemistry, N.R.C., for carrying out the X-ray diffraction examination.

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THERMODYNAMIC PROPERTIES OF BENZOIC ACID[1]

By R. Goton[2] and E. Whalley

The thermodynamic properties of benzoic acid were required in connection with its synthesis from benzene and carbon dioxide under high pressure. Accurate measurements of the heat of combustion and of the heat capacity have been made since the last reported thermodynamic study of Parks and Huffman (5), and we have recalculated these properties.

The heat capacity between 14° and 410° K. has been measured with considerable care on exceptionally pure samples by Ginnings and Furukawa (3). Their measurements appear to be much more accurate than previous ones (1) and were used exclusively. Likewise the heat of combustion when each of the gases involved is at its standard state (benzoic acid being at one atmosphere pressure) was determined very accurately by Jessup (4) and his value of $26{,}428.4 \pm 2.6$ int. j. gm.$^{-1}$ at 25° C., confirmed by Prozen and Rossini (7), is adopted.[3] The following conversion factors were used:

$$1 \text{ int. joule} = 1.000165 \text{ abs. joule}$$

and

$$1 \text{ abs. joule} = 0.239006 \text{ defined calorie.}$$

From the heat of combustion and the heats of formation of carbon dioxide (6) and water (8), we calculated the standard heat of formation of benzoic acid at 25° C. (298.15° K.), at the saturation pressure.[4] We found

$$(\Delta H_f^\circ)_{298.15} = -384{,}140 \pm 290 \text{ abs. j. mole}^{-1}.$$

The error involved in this quantity is twice the estimated standard error (9) calculated from measurements of each compound, applying the root-mean-square rule.

The heat capacity data of Ginnings and Furukawa are given at 5° intervals. The entropy was obtained at different temperatures by integrating C_p/T vs. T using Simpson's one-third rule. From the enthalpy function $(H_T^\circ - H_0^\circ)$ and the entropy, the free energy function $(F_T^\circ - H_0^\circ)$ was obtained. Dimensionless values of these quantities are given in Table I. (T_0 is the ice point temperature.) The accuracy is of the same order as that of the original heat capacity measurements. The precision between 60° and 395° K. is within 0.2%. Above 395° K. the results are less reliable (0.3%), benzoic acid being liquid (m.p. 395.52° K.) and possibly reacting with the containers. Between 60° and 14° K. the accuracy decreases to 1% because of uncertainties in the temperature measurements. In Table I, values at 298.15° K. and 395.52° K. were obtained by a graphical method. In Table II we give the conversion factors for different units.The molecular weight of benzoic acid has been taken as 122.12.

The standard heat of formation at 0° K. calculated from that at 298.15° K.,

[1]*Issued as N.R.C. No. 4065.*

[2]*National Research Council of Canada Postdoctorate Fellow 1955–56.*

[3]*A recent determination of the heat of combustion of benzoic acid (Coops, J., Adriaanse, N., and van Nes, K. Rec. trav. chim. 75: 237. 1956) agrees very well with previous measurements.*

[4]*The enthalpy difference between saturated pressure and one atmosphere is negligible.*

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TABLE I

T, ° K.	$\frac{(H_T°-H_0°)}{RT_0}$	$\frac{S°}{R}$	$\frac{-(F_T°-H_0°)}{RT}$	$\frac{-(\Delta F_f°)}{RT}$
100	1.544	7.503	3.285	405.2
150	3.160	10.74	4.986	252.5
200	5.202	14.26	6.154	175.6
220	6.146	14.76	7.135	153.0
240	7.165	16.31	8.154	135.7
260	8.264	17.89	9.207	121.3
280	9.442	18.68	9.467	108.3
298.15	10.58	20.15	10.45	99.77
300	10.70	20.26	10.52	98.92
310	11.36	20.85	10.84	93.74
320	12.04	21.44	11.16	88.42
330	12.74	22.03	11.48	83.15
340	13.46	22.62	11.80	79.88
350	14.21	23.20	12.15	76.30
360	14.97	23.79	12.43	73.38
370	15.75	24.67	13.04	69.27
380	16.56	25.55	13.65	65.76
390	17.38	26.43	14.05	62.20
395.52	17.85	26.46	14.13	61.75
395.52*	25.78	31.93	14.13	61.75
400*	26.27	32.79	14.84	60.20
410*	27.40	33.55	15.31	57.45

**Values at these temperatures are for the liquid.*

TABLE II

To convert tabulated value of	To	Having the dimensions indicated below	Multiply by
$S°/R$	$S°$	cal. deg.$^{-1}$ mole^{-1}	1.9871
$-(F_T°-H_0°)/RT$	$-(F_T°-H_0°)/T$	cal. gm.$^{-1}$ deg.$^{-1}$	0.016272
		abs. j. gm.$^{-1}$ deg.$^{-1}$	0.068083
$-(\Delta F_f°)_T/RT$	$-(\Delta F°)_T/T$	B.t.u. (lb. mole)$^{-1}$ deg.$^{-1}$	1.9858
		B.t.u. lb.$^{-1}$ deg.$^{-1}$	0.016261
$(H_T°-H_0°)/RT_0$	$(H_T°-H_0°)$	cal. mole^{-1}	542.80
		cal. gm.$^{-1}$	4.4448
		j. gm.$^{-1}$	18.597
		B.t.u. (lb. mole)$^{-1}$	976.38
		B.t.u. lb.$^{-1}$	7.9953

and the enthalpy function for benzoic acid, graphite (2), oxygen, and hydrogen (10), is

$$(\Delta H_f°)_0 = -366{,}761 \pm 310 \text{ abs. j. mole}^{-1}.$$

In the last column of Table I we give some values of the free energy of formation of benzoic acid, calculated from the free energy functions of the elements (References 2 and 10).

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OTTAWA, CANADA.

SEPARATION OF HIGH SPECIFIC ACTIVITY Na^{22} FROM IRRADIATED ALUMINUM[1]

BY N. HOLLBACH[2] AND L. YAFFE

Na^{22}, a positron emitter with a half-life of 2.6 years, is very useful as a tracer. It is however difficult to obtain in high specific activity. We have separated a high specific activity source and are reporting the method because of the general interest in this radionuclide.

Na^{22} may be produced in a cyclotron by the reaction $_{13}Al^{27}(p, 3p3n)_{11}Na^{22}$ (3). Preparation of a solution of high specific activity necessitates the separation of sodium from macro amounts of aluminum without the addition of a "carrier". This ruled out methods involving precipitation of the sodium. Precipitation of the aluminum was also ruled out because of excessive losses due to Na^{22} adsorption. The sinter–leach method (1) was not used because of the low yields suspected (4). The two methods remaining were (*a*) vacuum distillation and (*b*) ion exchange separation. The ion exchange method was chosen because of the relative speed, simplicity, and the quantitative nature of the separation.

In a study of the chemical composition of coal ash by Ellington and Stanley (2), a neutral solution of sodium and aluminum was adsorbed on a cation exchange resin. Elution with 0.4 *N* HCl caused the sodium to appear in the effluent while the aluminum remained adsorbed on the column. A variation of this method was adopted.

The irradiated 'spec-pure' aluminum was dissolved in a minimum amount of a mixture of concentrated hydrochloric acid and hydrogen peroxide which was gently warmed to hasten solution. The solution was evaporated until precipitation just commenced. The solution was cooled, diluted to 20 ml. with water triply-distilled from a quartz still, and concentrated ammonia added dropwise until the aluminum hydroxide precipitate persisted after 30 sec. of stirring. The precipitate was redissolved with a minimum of hydrochloric acid which had been diluted with the triply-distilled water, and the solution was adsorbed on an Amberlite IR-120 cation exchange resin. The column dimensions were 2.5 $cm.^2 \times 30$ cm. and a flow rate of 8 ml./min. was used.

[1]*With financial assistance from the National Research Council and the Atomic Energy Control Board.*
[2]*Holder of a Russell J. Eddy Award of the Chemical Institute of Canada, 1955.*

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SEPARATION OF HIGH SPECIFIC ACTIVITY Na^{22} FROM IRRADIATED ALUMINUM[1]

BY N. HOLLBACH[2] AND L. YAFFE

Na^{22}, a positron emitter with a half-life of 2.6 years, is very useful as a tracer. It is however difficult to obtain in high specific activity. We have separated a high specific activity source and are reporting the method because of the general interest in this radionuclide.

Na^{22} may be produced in a cyclotron by the reaction ${}_{13}Al^{27}(p, 3p3n)_{11}Na^{22}$ (3). Preparation of a solution of high specific activity necessitates the separation of sodium from macro amounts of aluminum without the addition of a "carrier". This ruled out methods involving precipitation of the sodium. Precipitation of the aluminum was also ruled out because of excessive losses due to Na^{22} adsorption. The sinter–leach method (1) was not used because of the low yields suspected (4). The two methods remaining were (*a*) vacuum distillation and (*b*) ion exchange separation. The ion exchange method was chosen because of the relative speed, simplicity, and the quantitative nature of the separation.

In a study of the chemical composition of coal ash by Ellington and Stanley (2), a neutral solution of sodium and aluminum was adsorbed on a cation exchange resin. Elution with 0.4 *N* HCl caused the sodium to appear in the effluent while the aluminum remained adsorbed on the column. A variation of this method was adopted.

The irradiated 'spec-pure' aluminum was dissolved in a minimum amount of a mixture of concentrated hydrochloric acid and hydrogen peroxide which was gently warmed to hasten solution. The solution was evaporated until precipitation just commenced. The solution was cooled, diluted to 20 ml. with water triply-distilled from a quartz still, and concentrated ammonia added dropwise until the aluminum hydroxide precipitate persisted after 30 sec. of stirring. The precipitate was redissolved with a minimum of hydrochloric acid which had been diluted with the triply-distilled water, and the solution was adsorbed on an Amberlite IR-120 cation exchange resin. The column dimensions were 2.5 $cm.^2 \times 30$ cm. and a flow rate of 8 ml./min. was used.

[1]*With financial assistance from the National Research Council and the Atomic Energy Control Board.*
[2]*Holder of a Russell J. Eddy Award of the Chemical Institute of Canada, 1955.*

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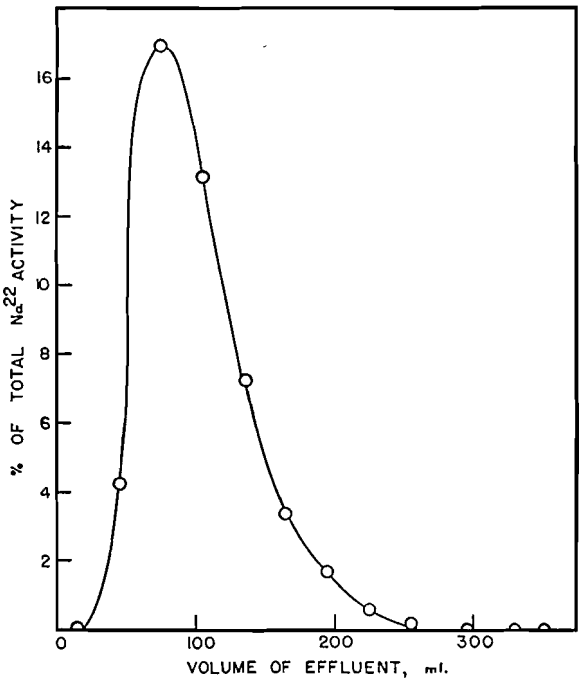

FIG. 1. Separation of Na^{22} from aluminum using Amberlite IR-120.

The sodium was eluted from the resin with 0.4 *N* hydrochloric acid. The first 270 ml. contained 100% of the sodium and the results are shown in Fig. 1. The solution was evaporated to about 1 ml. and again passed through the regenerated resin. The resulting solution was evaporated to dryness. The residue (~10 mgm.) contained organic matter from the resin, ammonium chloride, and a small amount of hydrated aluminum oxide. The residue was treated with concentrated nitric acid and taken to dryness several times to destroy organic matter, converted to the chloride, and heated strongly to volatilize ammonium chloride. The residue (aluminum oxide) was leached with cold water. The centrifugate from five washings contained 99.8% of the original Na^{22} activity and was radiochemically pure.

The specific activity of an evaporated sample of the solution was of the order of 0.1 microcurie per microgram and could obviously be increased.

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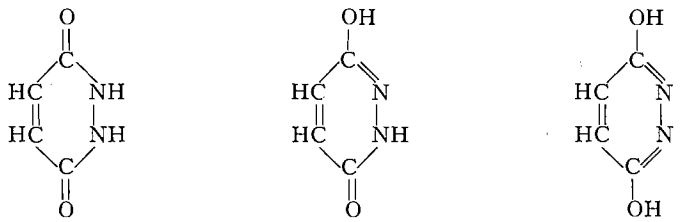
THE STRUCTURE OF MALEIC HYDRAZIDE AS INFERRED FROM THE ULTRAVIOLET SPECTRA OF ITS METHYL DERIVATIVES[1]

By D. M. Miller and Robert W. White

Maleic hydrazide (MH) exhibits acidic properties and has been shown to have a single pK_a of 5.65 (4). It has also been shown (4) to have two spectra, one at low pH (A) and one at high pH (B). There are three possible tautomeric forms for MH:



I II III

so that spectrum A may be assigned to structure I, II, or III while the ionized form of II or III may account for the B spectrum. Arndt, Loewe, and Ergener (1), however, have shown that structure III is unlikely since the reaction of O-methyl maleic hydrazide (IV) with an excess of diazomethane gave the O,N-dimethyl maleic hydrazide (V) but no O,O′-dimethyl (VI) product. A study of the ultraviolet spectra of several methyl derivatives of MH has been undertaken in this laboratory to gain information about the various possible structural forms, and the results are given here.

The methyl derivatives investigated and the methods of their synthesis are as follows:

6-methoxy-3(2H)pyridazinone (IV),
6-methoxy-2-methyl-3(2H)pyridazinone (V),
3,6-dimethoxypyridazine (VI),
6-hydroxy-2-methyl-3(2H)pyridazinone (VII),
1,2-dimethyl-3,6(1H,2H)pyridazinedione (VIII).

Compound IV was obtained in low yield by the reaction of methyl iodide on the silver salt of MH (5); V, VII, and VIII were all prepared according to the methods of Eichenberger, Staeheim, and Druey (3); and VI was made according to the directions of Druey, Meier, and Eichenberger (2).

Technical maleic hydrazide obtained from Naugatuck Chemicals, Elmira, Ontario, was twice recrystallized from water giving a crystalline product melting at 296° C.

The ultraviolet spectra reproduced in Fig. 1 were obtained on a Beckman

[1]*Contribution No. 80, Science Service Laboratory, London, Ontario.*

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Model DK-1 recording spectrophotometer and were made on solutions of concentration 5×10^{-5} *M* at two pH's for each compound as follows:

A—0.1 *N* HCl,

B—$Na_4P_2O_7$ buffer at pH 8.40.

The two spectra for IV, V, and VIII were found to coincide while separate spectra were found for the others. The similarity between the spectra of MH and VII is obvious. For the sake of comparison each of the other spectra has superimposed on it (as a broken line) that spectrum of MH most closely resembling it.

Titration curves of aqueous solutions of each of the compounds were obtained. The only methyl derivatives showing inflection points were VII for which a pK_a of 5.65 was found (identical to that of MH), and VI for which a pK_b of 12.0 was found.

The dimethyl derivatives, VIII, V, and VI, have configurations similar to structures I, II, and III respectively, while of the monomethyl derivatives, VII may have configuration I or II and IV, II or III. Comparing now spectrum A for unionized MH with the other spectra in Fig. 1 it can be seen

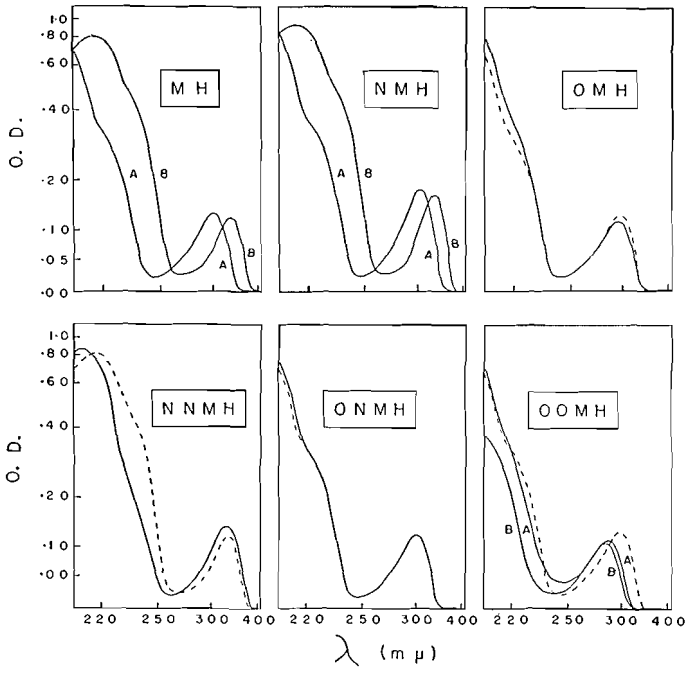

FIG. 1. Ultraviolet spectra of MH and its methyl derivatives.
NMH, VII; OMH, IV; NNMH, VIII; ONMH, V; OOMH, VI.

that it is similar only to the spectra of IV, V, and VII, the compounds capable of existing in form II. On the other hand, spectrum B for the ionized form of MH shows a similarity only to that of VII, the one derivative capable of ionizing as an acid.

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The similarity between the ultraviolet spectra, pK_a values, and chemical reactivities of MH and VII could only arise from a similarity in structure. This fact added to the other evidence presented here leads to the conclusion that MH exists as structure II, i.e. 6-hydroxy-3(2H)pyridazinone.

We wish to thank Dr. F. Arndt for his useful suggestions concerning the synthesis of IV and Dr. J. Druey for a sample of this compound, also Dr. G. D. Thorn for helpful discussion and Mr. B. Huston for technical assistance.

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5. Unpublished results. See also Ref. 1 for an alternative method.

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THE RELATION BETWEEN ACTIVATION ENERGY OF THE VISCOSITY AND HEAT OF VAPORIZATION FOR MOLTEN SALTS[1]

BY F. VAN ZEGGEREN[2]

The temperature dependence of the viscosity of a liquid is expressed in the formula

$$\eta = B \exp(E_{vls}/RT)$$

where η is the viscosity, E_{vls} the so-called activation energy of the viscosity, B a constant, and R and T have their usual significance. This formula can be derived theoretically by applying the theory of absolute reaction rates to the problem of viscosity (4).

Since in viscous flow holes have to be available of the size of the atom or molecule in the activated state, i.e. on top of the barrier which corresponds with E_{vls}, and the work necessary to form a hole of molecular size in the liquid is the energy of vaporization ΔE_{vap}, E_{vls} must be a fraction of ΔE_{vap}. For a large number of liquids the ratio $\Delta E_{vap}/E_{vls}$ has been determined, and the important conclusion is that

$$C = \Delta E_{vap}/E_{vls}$$

is a constant for all "normal" liquids. The value of the constant C is 3.5 ± 0.5.

For liquids such as molten metals this ratio of the heat of vaporization to the activation energy of the viscous flow has also been determined (3), but much too large values have been found, viz. varying between 8 and 25 or more.

[1]*Issued as N.R.C. No. 4073.*
[2]*National Research Council Postdoctorate Fellow 1955–.*

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However, Ewell and Eyring (3) showed that this can be accounted for by the difference in mechanism between the two processes: vaporization and viscous flow. In vaporization the neutral metal atoms are the units which contribute to ΔE_{vap}, whereas in viscous flow the energy barrier E_{vis} corresponds with the metal ions, stripped of their conductance electron (s). The barrier is not influenced by the moving electrons. In correcting their ratio values with a factor that takes this difference into account, they obtained for the quantity

$$C = \frac{\Delta E_{vap}}{E_{vis}} \times \frac{\text{vol. of ion}}{\text{vol. of atom}}$$

or

$$C = \frac{\Delta E_{vap}}{E_{vis}} \times \frac{(r_{ion})^3}{(r_{atom})^3}$$

a constant value, which is the same as found for the normal liquids, viz. 3.5 ± 0.7.

It seemed interesting to investigate if an analogous relation holds for the molten salts.

For a large number of molten salts the relationship between viscosity (or fluidity) and the number of holes in the melt is supported by the fact that for these salts the relation of Batschinski

$$\eta = a/(V - V_s)$$

is valid, as is the case for normal liquids (1). In this formula η is the viscosity, V and V_s are the molar volumes of liquid and unexpanded solid respectively, and a is a constant. Thus the hole theory of liquids can also be applied in this case. Indeed, Bloom and Heymann (2) were able to show that the relation $\eta = B \exp(E_{vis}/RT)$ also holds for fused salts.

Assuming that the molecule is the unit that evaporates, and that both positive and negative ions have to cross the energy barrier for the viscous flow, the correction factor would be

$$[\tfrac{4}{3}\pi(r_+)^3 + \tfrac{4}{3}\pi(r_-)^3]/V_{mol}$$

where r_+ and r_- are the radii of positive and negative ions respectively, and V_{mol} is the volume of the molecule. Thus:

$$C = \frac{\Delta E_{vap}}{E_{vis}} \times \frac{\tfrac{4}{3}\pi(r_+^3 + r_-^3)}{V_{mol}}.$$

E_{vis} has been determined for a few salts by Bloom and Heymann (2), ΔE_{vap} for these compounds is given by Herz (5). In Table I values of ΔE_{vap}, E_{vis}, $\frac{4}{3}\pi(r_+^3 + r_-^3)$, V_{mol}, and C are tabulated for a number of alkali halides. Bloom and Heymann expressed some doubt about the value for E_{vis} of LiBr and indeed for this salt an extremely high value for C is found. Nevertheless, taking this value into account, it can be said that C is a constant, with an average value of 3.1 (± 0.5), which proves that a molten salt can be considered as a normal liquid in the same sense as, for example, a molten metal.

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TABLE I

Salt	ΔE_{vap} in kcal./mole	E_{vis} in kcal./mole	$^4/_3\pi(r_+^3+r_-^3)$ in Å^3	V_{mol} in Å^3	C
LiCl	37.7	8.8	25.8	34.0	3.3
NaCl	44.4	9.4	28.5	44.8	3.0
KCl	40.4	7.8	34.7	62.4	2.9
LiBr	35.7	6.0(?)	32.1	41.6	4.6
NaBr	38.6	10.6	34.8	53.3	2.4
KBr	38.4	7.9	41.0	71.9	2.8
NaI	39.0	7.4	46.5	67.9	3.6
KI	37.2	9.2	52.7	88.0	2.4

ACKNOWLEDGMENT

The author wishes to thank Dr. G. C. Benson for his interest in this work.

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NUCLEAR MAGNETIC RESONANCE STUDY OF PHASE TRANSITIONS IN ANHYDROUS SODIUM STEARATE

BY R. F. GRANT,[1] N. HEDGECOCK,[2] AND B. A. DUNELL[1]

The investigation of mesomorphic phase transitions in sodium stearate has been made by a number of workers using several techniques. Puddington and his co-workers (2, 5, 8, 9, 10) have studied the variation of viscosity, density, and light transmission with temperature, and R. and M. Vold with their co-workers (11, 12, 13, 14, 15) have studied the density, heat capacity, and electrical conductivity of sodium stearate and observed phase transitions optically using the "hot wire" technique. Table I lists the main phase transitions that have been observed in anhydrous sodium stearate and shows the range of temperatures within which each transition has been reported.

Interpretation of the molecular mechanisms of these transitions has been assisted by X-ray diffraction studies on sodium stearate (3, 4, 7). It is considered that each transition represents a change in the degree of freedom of rotational motion of the hydrocarbon part of the molecule or a change in the ability of the polar end to reorient, the low temperature transitions being associated with rearrangement of the hydrocarbon chains, and the high

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TABLE I

PHASE TRANSITIONS IN ANHYDROUS SODIUM STEARATE

Transition	Range of reported temperatures, ° C.	References
Genotypical point	65–70	9, 13
Curd to supercurd	89–93	11, 14
Supercurd to subwaxy	110–117	9, 13
Subwaxy to waxy	125–135	2, 10, 13, 14
Waxy to superwaxy	165–168	2, 11, 12
Superwaxy to subneat	189–209	10, 11, 12, 13
Subneat to neat	226–262	10, 11, 12, 13, 15
Melting point	278–290	8, 12, 15

temperature transitions being associated with reorientation of the polar ends of the molecules. Investigation of line width in nuclear magnetic resonance studies gives an indication of the extent of molecular rotation and reorientation in the solid state (1). A study has been started, therefore, of the nuclear magnetic resonance spectrum of sodium stearate over a range of temperatures within which phase changes are observed.

The sodium stearate used in this investigation was prepared from Eastman Kodak white label stearic acid by two methods, following the procedure of Stainsby, Farnand, and Puddington (10). In one procedure, stearic acid dissolved in hot 95% ethanol was titrated with a saturated 95% ethanol solution of sodium hydroxide to two or three drops beyond a phenolphthalein end point, and in the other, stearic acid dissolved in hot absolute ethanol was titrated just beyond a phenolphthalein end point with a 3% solution of sodium ethoxide in absolute ethanol. In both cases the indicator was used externally. The dried sodium stearate crystals, sealed in melting point tubes, became translucent at 130° C. and became transparent and showed a meniscus at 262° C., in agreement with the behavior reported by M. and R. Vold (11, 13). The sodium stearate samples used in the experiments were melted in sample bulbs under vacuum. Dry nitrogen was then introduced into the vacuum system and the sample bulb sealed off and detached from the vacuum system.

The sample and nuclear magnetic resonance spectrometer probe were immersed in a thermostat which consisted of a dewar vessel filled with nujol heated by an immersion knife-heater. The magnet and recording apparatus used were those described by Waterman and Volkoff in a recent paper (16). The remainder of the spectrometer was an adaptation of one described by Gutowsky, Meyer, and McClure (6). Line width was taken as the separation in gauss of the points of maximum slope on the absorption signal, and was measured in an experiment in which the sodium stearate sample was heated slowly to the required temperature and maintained at that temperature for 30 min. before the absorption signal was recorded.

In Fig. 1, the line width is plotted as a function of temperature for the two samples of sodium stearate prepared in the two ways described above. No distinction in behavior was observable for the two samples. The line width vs. temperature curve shows three discontinuities between 20° C. and 200° C.

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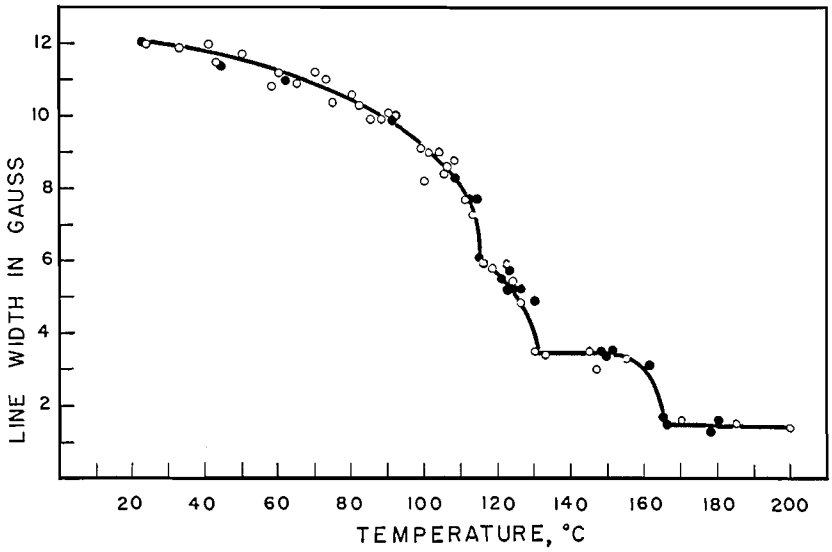

FIG. 1. Variation of line width with temperature for sodium stearate. Open circles: Sample prepared by neutralization of stearic acid with sodium hydroxide. Filled circles: Sample prepared by neutralization of stearic acid with sodium ethoxide.

These correspond to observed transitions at 114° C., 130° C., and 165° C., although it may reasonably be claimed that the presence of a transition at 114° C. is not unequivocally shown by these results. Comparison of our observed transition temperatures with some of those of other workers is shown in Table II. A satisfactory discussion of the significance of these results in

TABLE II

COMPARISON OF TRANSITION TEMPERATURES OBSERVED IN THIS WORK WITH THOSE OBSERVED BY OTHER METHODS

Transition	Method and temperature				
	Calorimeter (13)	Hot wire (11)	Dilatometer (12)	Light transmission (2)	N.M.R.* this work
Supercurd to subwaxy	114	—	117	—	114
Subwaxy to waxy	134	132	132	132	130
Waxy to superwaxy	—	167	—	165	165

**Nuclear magnetic resonance.*

terms of molecular motion requires the calculation of the second moments of the line shapes. The absorption signals from which these results are taken have not proved satisfactory for this purpose since they were obtained primarily to measure line width. Work is in progress, however, to determine the second moments of the line shapes for sodium stearate and other fatty acid salts.

We are indebted to Drs. G. M. Volkoff and G. M. Shrum of the Physics Department of this university for their co-operation in making the facilities

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of their department available to us for doing these experiments. We also wish to thank the National Research Council of Canada for Grant G. 304 which has made this work possible.

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LYCOPODIUM ALKALOIDS

IV. REACTIONS OF α-CYANOBROMOLYCOPODINE AND ITS DERIVATIVES[1]

BY L. R. C. BARCLAY[2] AND DAVID B. MACLEAN

ABSTRACT

The hydrogenolysis and hydrolysis of α-cyanobromolycopodine to the secondary tricyclic base, α-des-dihydrolycopodine, is reported. The latter compound was converted to the methiodide in poor yield so that further degradations of the molecule through this derivative were not feasible. Hydride reductions of α-cyanobromolycopodine and some of its derivatives are recorded. The presence of a methylene group adjacent to the carbonyl group in lycopodine has been proved. Evidence is presented which suggests that the carbonyl group and the nitrogen atom are relatively close to one another in the molecule.

In a previous communication, MacLean, Manske, and Marion (4) reported the reaction of lycopodine with cyanogen bromide. They isolated two isomeric cleavage products, designated α- and β-cyanobromolycopodine. The α-isomer was formed in predominant amount. A number of reactions of these compounds were studied and from their work it was found that α-cyanobromolycopodine was a primary bromide.

In this investigation the study of the reactions of α-cyanobromolycopodine was extended in the expectation that more information concerning the ring structure of the alkaloid would be obtained. In this respect our work has been only moderately successful, but a number of new derivatives of interest for further study have been prepared.

Lycopodine was isolated from the crude mixed alkaloids from several plant sources by a convenient procedure outlined in the experimental section. The procedure for conversion to the isomeric cyanobromides has also been improved and reported. α-Cyanobromolycopodine, the major product, was converted to α-cyanolycopodine by the method reported previously (4). Hydrolysis of α-cyanolycopodine, $C_{17}H_{26}ON_2$, yielded the secondary base α-des-dihydrolycopodine, $C_{16}H_{27}ON$, which showed absorption in the =NH region of the infrared spectrum. This secondary base was acylated with acetic anhydride to a neutral amorphous compound which no longer showed =NH absorption but had a band at 1640 cm.$^{-1}$ in the amide region of the infrared. It was also methylated by formaldehyde and formic acid to a tertiary base

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which analyzed for a single =N—CH_3 group. Conversion of the tertiary base to the quaternary salt by methyl iodide proceeded in very poor yield. An attempt to carry out a reductive fission of the quaternary salt was not successful. Other degradations of the methiodide were not attempted because of the low over-all yields obtained in the conversion of α-cyanolycopodine to the methiodide. No satisfactory explanation can be offered for the failure of the secondary base to alkylate readily with alkyl halides nor of the tertiary N-methyl base to form a methiodide readily. Lycopodine, on the other hand, formed a methiodide rapidly and quantitatively when an acetone solution of the base was mixed with methyl iodide.

A number of hydride reductions were carried out on α-cyanobromolycopodine and its derivatives to prepare compounds for dehydrogenation and other degradation studies now in progress. The secondary base, $C_{16}H_{27}ON$, was converted to the corresponding carbinol, $C_{16}H_{29}ON$, by lithium aluminum hydride. An alternative and more convenient preparation of this carbinol resulted from the direct reduction of α-cyanobromolycopodine with lithium aluminum hydride. In this conversion the bromine underwent hydrogenolysis, the carbonyl group was reduced, and the =N—CN linkage was converted to =NH. Some neutral material was also derived as a by-product of this reduction in which the =N—CN grouping was still present. This material proved to be the corresponding cyanamide, $C_{17}H_{28}ON_2$, which was also derived by two alternative procedures. The Meerwein–Ponndorf reduction of α-cyanolycopodine was slow and inefficient, but reduction of α-cyanobromolycopodine with sodium borohydride proceeded readily to give a good yield of the compound $C_{17}H_{28}ON_2$.

The displacement of bromine by hydrogen in the sodium borohydride reduction is somewhat unusual since this reagent does not ordinarily affect carbon–halogen linkages under these mild conditions. Since the reaction has been carried out several times with the same result, it would appear that this is an authentic case of a sodium borohydride reduction of an aliphatic halogen.

The bromination of α-cyanolycopodine was studied in an attempt to prepare derivatives of the compound suitable for oxidative degradation. In carbon tetrachloride solution α-cyanolycopodine readily consumed bromine with deposition of a solid amorphous precipitate. From this precipitate it was possible to isolate, although in low yield, a monobromo derivative. The carbonyl absorption in the infrared of this brominated derivative was displaced by 10 $cm.^{-1}$ to 1710 $cm.^{-1}$ in comparison to the starting material at 1700 $cm.^{-1}$. Such a shift is consistent for an α-bromoketone (1). In contact with water or aqueous alkali this product readily lost its bromine to produce a mixture of compounds probably alcoholic and olefinic in nature.

The main product of the bromination reaction was amorphous, and despite repeated attempts, it could not be induced to crystallize. In common with the monobrominated compound it readily lost its bromine in contact with aqueous alkali. Treatment of these amorphous residues with alkaline aqueous dioxane yielded a product from which a crystalline derivative was obtained.

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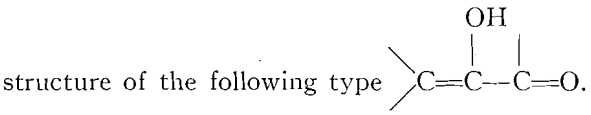
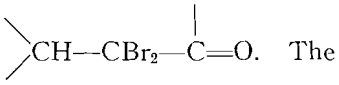
This compound, which analyzed for $C_{17}H_{24}O_2N_2$, had the properties of an enol. The infrared spectrum indicated the presence of a conjugated carbonyl group, an olefinic double bond, and an hydroxyl group. The ultraviolet absorption spectrum showed strong absorption at 2800 Å which is indicative of an hydroxylated α,β-unsaturated carbonyl chromophore (3). The analytical and spectral results suggested a structure of the following type  . Such a structure would arise from an α,α-dibrominated ketone,  . The bromination reaction thus proceeded to give a mixture of mono- and di-brominated ketone.

The failure of lycopodine to form a benzal derivative (2) is at variance with the above results and we considered them suspect for this reason. However, α-cyanolycopodine formed a monobenzal derivative, $C_{24}H_{30}ON_2$, and the presence of a methylene group adjacent to the carbonyl group was confirmed. Under similar conditions, lycopodine failed to react in confirmation of the work of Douglas *et al.* quoted above. One must therefore conclude that this methylene group occupied a hindered position in lycopodine and the hindrance was relieved on ring fission in the formation of α-cyanolycopodine.

The ease with which α-cyanolycopodine brominated led us to investigate the bromination of lycopodine and α-des-dihydrolycopodine. Both the bases readily formed monobromo derivatives isolated as their hydrobromides. Both of these brominated hydrobromides underwent decomposition on conversion to the free bases and no identifiable fragments could be isolated from either substance. Since both these compounds gave a Fehling's test, they are undoubtedly α-bromoketones. The pK_a of these bromo compounds was determined and compared with the parent bases and the dihydro bases. These results are summarized below:

lycopodine	9.06
dihydrolycopodine	9.2(2)
bromolycopodine	7.30
α-des-dihydrolycopodine	9.05
α-des-tetrahydrolycopodine	9.80
bromo-α-des-dihydrolycopodine	7.20

The similarity in pK_a of lycopodine and α-des-dihydrolycopodine suggests that in the ring fission reaction the relationship of the nitrogen and carbonyl groups has not been altered. The increase in pK_a on reduction of these compounds is probably not significant. However, the greatly decreased basicity of the brominated bases implies a rather close proximity of the carbonyl and nitrogen atoms in the molecule.

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EXPERIMENTAL

Lycopodine

Three plant species, *L. clavatum*, *L. obscurum*, and *L. tristachyum*, were used as a source of lycopodine. The plant materials were extracted by the method of Manske and Marion (5). In all cases lycopodine was derived from the crude alkaloids of these plant extracts by chromatography on alumina using chloroform as eluant. Lycopodine passed rapidly through the column and was thus separated from other alkaloid constituents. Final purification was achieved through conversion to the perchlorate.

The pK_a of lycopodine was determined by the titration of the perchlorate and the hydrobromide in 50% methanol–water. Values obtained were 9.06 and 9.07, respectively.

Reaction of Lycopodine with Cyanogen Bromide

Lycopodine (15 gm.) dissolved in 150 ml. of dry benzene was added over a period of 10 hr. with stirring to a solution of 50 gm. of cyanogen bromide in 150 ml. of dry benzene. The reaction mixture was then allowed to stand overnight. The benzene and the excess cyanogen bromide were removed under vacuum. The residue was taken up in chloroform, washed with dilute acid, water, and dilute sodium bicarbonate. The acidic and aqueous washings were saved and 1.2 gm. lycopodine was reclaimed therefrom. The chloroform solution was concentrated and adsorbed on a column of alumina. Elution with chloroform yielded a first fraction of cyanobromides (18.9 gm.) which crystallized in contact with ether. Following the cyanobromides down the column was a distinct brown band which yielded an amorphous residue. This residue showed strong absorption in the hydroxyl region as well as the carbonyl and nitrile region. This residue (1.0 gm.), on acetylation, yielded a crystalline O-acetyl derivative identical to α-cyanoacetoxylycopodine reported previously (4).

The cyanobromide residues were crystallized from ether. The first crop of crystals consisted of pure α-cyanobromolycopodine, m.p. 140–141°.[3] Yield = 8.8 gm. Concentration of the mother liquors yielded crystalline material which melted over a wide range and was a mixture of the α- and β-cyanobromides. By repeated recrystallizations it was possible to isolate additional crops of the pure α- and in some cases the pure β-isomer, although these cases were rare and perhaps fortuitous. Pure β-isomer was obtained in many cases by manual separation of the crystals, which have distinctly different forms; the α-isomer crystallized in pyramidal form, the β-isomer in needles. Fortunately it was possible to convert this mixture into separable derivatives of use in other investigations under way in these laboratories. The pure β-cyanobromolycopodine melted at 106–108°.

Both isomers exhibit strong absorption in the infrared[4] at 1700 cm.$^{-1}$ in the carbonyl region and at 2200 cm.$^{-1}$ in the —C≡N region. There are distinct differences in the 600–1200 cm.$^{-1}$ region.

[3]*All melting points are corrected.*

[4]*Infrared spectra were carried out in nujol mull unless otherwise specified and were determined on a Perkin-Elmer No. 21 recording spectrophotometer with a sodium chloride prism.*

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Hydrolysis of α-Cyanolycopodine

α-Cyanolycopodine (0.5 gm.), prepared by the method of MacLean, Manske, and Marion (4), was refluxed overnight with 20 ml. of 2 *M* hydrochloric acid containing 5 ml. of *n*-propanol to ensure partial solution. The clear solution, concentrated to remove the alcohol, deposited crystals of the hydrochloride upon cooling. After recrystallization from methanol, the hydrochloride melted above 300°.

Calc. for $C_{16}H_{27}ON.HCl$: C, 67.23; H, 9.81; N, 4.90.
Found: C, 66.88, 66.92; H, 9.76, 9.78; N, 4.84, 4.72%.
pK_a (50% methanol–water) = 9.05.

The free base, obtained from the hydrochloride, was a solid, difficult to obtain in pure form, which softened at 45° and melted at 49° after repeated crystallizations from hexane. Its infrared absorption spectrum contained no bands in the nitrile region, but had the usual carbonyl band at 1694 cm.$^{-1}$ and a strong band at 3330 cm.$^{-1}$, indicative of an =NH grouping.

Reaction of α-Des-dihydrolycopodine with Acetic Anhydride

α-Des-dihydrolycopodine (0.1 gm.) was dissolved in a few cubic centimeters of acetic anhydride and the solution heated on the steam cone in the presence of anhydrous sodium acetate. After removal of excess acetic anhydride under vacuum, the residue was treated with ether and the ether solution washed with dilute hydrochloric acid, sodium bicarbonate, and water. Upon distillation of the ether there remained an amorphous solid. This material did not crystallize from the usual solvents. However, the infrared absorption spectrum contained a strong band at 1640 cm.$^{-1}$ which, together with the absence of absorption in the =N—H region, is indicative of an acetyl derivative. The usual carbonyl band appeared at 1700 cm.$^{-1}$.

Alkylation of α-Des-dihydrolycopodine

A mixture of α-des-dihydrolycopodine (0.79 gm.), formic acid (0.16 cc., 90%), and formaldehyde (0.9 cc.) was heated under reflux on the steam bath for 10 hr. The initial reaction, which was vigorous and accompanied with foaming, subsided after one to two hours. At the end of the reaction time the mixture was diluted with water, made strongly acid with hydrochloric acid, and extracted with ether. The aqueous layer was separated, made alkaline with ammonia, and extracted several times with ether. Distillation of the ether yielded a viscous oil with no absorption in the 3300–3400 cm.$^{-1}$ region, indicative of transformation of the secondary α-des-dihydrolycopodine to a tertiary base. The carbonyl band was not shifted.

This tertiary base was dissolved in a small volume of acetone and treated with concentrated hydrochloric acid, which initiated immediate crystallization of the hydrochloride as near colorless prisms, m.p. 254°. Recrystallization from acetone yielded prisms, m.p. 256°. Yield = 0.52 gm.

Calc. for $C_{17}H_{29}ON.HCl.H_2O$: C, 64.22; H, 10.14; N, 4.20; NCH_3, 9.14.
Found: C, 64.49, 63.84; H, 9.94, 9.91; N, 4.65, 4.84; NCH_3, 9.55, 9.65.

Alkylation of α-des-dihydrolycopodine with methyl iodide and methyl

sulphate was not satisfactory, nor would the base react with butyl bromide in a sealed tube at 150°.

Methiodide of the Tertiary Base

A sample of the tertiary base (0.33 gm.) was added to excess methyl iodide and the solution refluxed on the steam bath. After about three hours a small yield of crystals was obtained. After further refluxing for 20 hr., more crystals formed, but the total yield was very low—approximately 10%. Recrystallization of the combined lots of crystals from a mixture of methanol and ethyl acetate produced colorless crystals, m.p. 192.5°.

Calc. for $C_{18}H_{32}ONI$: C, 53.33; H, 7.96; N, 3.46.

Found: C, 53.43, 53.30; H, 8.12, 7.95; N, 3.24, 3.14.

A small sample of the methiodide was dissolved in methanol, platinum oxide was added, and the mixture treated with hydrogen at 40 p.s.i.g. for eight hours. The unreacted methiodide was recovered on removal of the methanol and addition of ethyl acetate to the residue.

Lithium Aluminum Hydride Reduction of α-Des-dihydrolycopodine

Lithium aluminum hydride (1.0 gm.) was added to anhydrous ether in a three-necked flask fitted with a reflux condenser and dropping funnel, and the mixture refluxed for three hours. A solution of the α-des-dihydrolycopodine (3.0 gm.) in anhydrous ether was then added over a one-hour period with vigorous stirring. The mixture was stirred for an additional two hours before decomposition—first with moist ether, then with water. The ether layer was separated and distillation of the ether produced a crystalline product (2.0 gm., 66%). Recrystallization from ether yielded colorless crystals, m.p. 168–169°.

Calc. for $C_{16}H_{29}ON$: C, 76.43; H, 11.63; N, 5.58.

Found: C, 76.15, 76.05; H, 11.67, 11.55; N, 5.75, 5.79.

pK_a (50% methanol–water) = 9.80.

The infrared spectrum of this compound showed absorption at 3150 $cm.^{-1}$ and no carbonyl absorption.

Lithium Aluminum Hydride Reduction of α-Cyanobromolycopodine

An ethereal solution of α-cyanobromolycopodine (3.0 gm.) was added slowly with stirring to 200 cc. of ether containing 22 cc. of approximately 0.1% lithium aluminum hydride solution. The stirring and refluxing was continued for eight hours, and after the reaction mixture had been left for 14 hr., it was decomposed with moist ether. The ether layer was extracted repeatedly with dilute hydrochloric acid to remove the basic fraction. A small amount of non-basic material (0.18 gm.) was isolated on evaporation of the ether. A portion of this non-basic material was similar to the Meerwein–Ponndorf reduction product of α-cyanolycopodine reported below.

The above hydrochloric acid extract was made alkaline with ammonia and extracted repeatedly with ether and finally with chloroform in a continuous extractor. Removal of the ether–chloroform solvent left a crystalline residue (1.75 gm., 82%). Recrystallization from ether produced colorless crystals, m.p. 168–169°, which did not depress the melting point of the alcohol formed on lithium aluminum hydride reduction of α-des-dihydrolycopodine.

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Reaction of α-Cyanolycopodine with Aluminum Isopropoxide

α-Cyanolycopodine (0.62 gm.) was dissolved in dry isopropyl alcohol, freshly prepared aluminum isopropoxide (2 gm.) was added, and the solution heated under reflux. The top of the reflux condenser was fitted with a trap containing a side arm with a stopcock and a cold finger filled with ethanol. The cold finger served to condense most of the refluxing isopropyl alcohol so that the distillation of the solvent along with any acetone formed was carried out at a slow, constant rate.

After several days the reaction mixture was worked up to yield a semi-crystalline residue. On addition of ether, immediate separation of colorless crystals occurred. After recrystallization from ether they melted at 191–192°.

Calc. for $C_{17}H_{28}ON_2$: C, 73.87; H, 10.21; N, 10.1.

Found: C, 73.84, 73.67; H, 9.77, 10.15; N, 8.99, 9.05.

Reaction of α-Cyanobromolycopodine with Sodium Borohydride

A solution of α-cyanobromolycopodine (4.0 gm.) in ethanol was added with stirring to a warm solution of sodium borohydride (6.0 gm.) in ethanol. After the mixture had been allowed to stand for one day, the excess sodium borohydride was destroyed with formaldehyde. The mixture was made just acid with hydrochloric acid, the solvent removed under vacuum, and the residue was extracted with chloroform. The chloroform extract was washed with dilute acid, sodium bicarbonate, and water. Evaporation of the chloroform yielded a crystalline product (3.0 gm., 97%) which was identical by mixed melting point and infrared spectrum to the product prepared by the reduction of α-cyanolycopodine with aluminum isopropoxide.

Reaction of α-Cyanolycopodine with Bromine in Carbon Tetrachloride

α-Cyanolycopodine (0.72 gm.) was dissolved in dry carbon tetrachloride in a three-necked flask provided with a stirrer and dropping funnel. Bromine (5%) in carbon tetrachloride was added slowly with stirring. After a few minutes the uptake of bromine was rapid and precipitation occurred. A total of 8 cc. of the bromine solution was added. At the end of the reaction a portion of the yellow precipitate was separated by filtration. This material rapidly became amorphous on being left to stand, and attempts to crystallize it from various solvents were unsuccessful. Chloroform was added to make a clear solution and the excess bromine destroyed by washing with bisulphite solution. Removal of the solvent under vacuum left an amorphous residue from which a crystalline product (0.17 gm.) separated on the addition of ether. Recrystallization from an acetone–ether mixture yielded colorless crystals which began to decompose at 122° and melted at 129°.

Calc. for $C_{17}H_{25}ON_2Br$: C, 57.79; H, 7.14; N, 7.94; Br, 22.6.

Found: C, 58.16, 57.99; H, 7.29, 7.16; N, 7.90, 7.82; Br, 21.8, 22.0.

The infrared spectrum of this brominated compound showed absorption in the nitrile region at 2210 $cm.^{-1}$ and the carbonyl region at 1710 $cm.^{-1}$, while the starting material had carbonyl absorption at 1700 $cm.^{-1}$.

Upon distillation of the solvent from the mother liquor of the above bromo compound, there was obtained 0.74 gm. of amorphous residue. The infrared

spectrum of this residue showed weak bands at 3400 cm.$^{-1}$ and 1630 cm.$^{-1}$ in addition to the bands at 1710 cm.$^{-1}$ and 2210 cm.$^{-1}$ for the crystalline bromo compound.

The crystalline monobromo compound reacted readily with aqueous alkali and silver oxide to yield a mixture of products. Examination of the mixture in the infrared indicated the presence of hydroxyl and conjugated carbonyl groups.

The Action of Alkali in Aqueous Dioxane on Crude Bromination Product

The non-crystalline bromination product (0.6 gm.) was heated on the steam bath in 5% potassium hydroxide containing some purified dioxane to cause partial solution. The reaction mixture soon became very dark in color and the heating was discontinued. The mixture was concentrated under vacuum to remove the dioxane and then extracted with ether. The ether extract was washed with water, acid, and alkali to yield only 0.13 gm. of non-crystalline product which was not further investigated. The aqueous layer was therefore acidified and chloroform extracted to yield a crystalline product (0.2 gm.) which melted at 157–158° after recrystallization from ether – petroleum ether.

Calc. for $C_{17}H_{24}O_2N_2$: C, 70.79; H, 8.39; N, 9.71.

Found: C, 70.76, 70.69; H, 8.35, 8.32; N, 9.25, 9.35.

The infrared spectrum of this compound had bands at 1640 cm.$^{-1}$, 1660 cm.$^{-1}$, 2210 cm.$^{-1}$, and 3340 cm.$^{-1}$. The ultraviolet spectrum showed λ_{max} = 2800 Å, log ϵ = 4. The compound gave a deep blue coloration with ferric chloride in aqueous ethanol.

Bromination of Lycopodine

A solution of 1.00 gm. of lycopodine was added with vigorous stirring to an equimolar amount of bromine dissolved in carbon tetrachloride. The uptake of bromine was very rapid at room temperature and enough additional solvent was added to redissolve the hydrobromide salt which initially precipitated.

The reaction mixture was allowed to stand overnight and the solvent removed under vacuum on the steam cone to produce a theoretical yield of bromolycopodinehydrobromide. Recrystallization from acetone–methanol yielded colorless crystals which melted at 290–295° (dec.).

Calc. for $C_{16}H_{24}ONBr.HBr$: C, 47.20; H, 6.19; N, 3.44; Br, 39.2.

Found: C, 48.64, 48.64; H, 6.25, 6.32; N, 3.67, 3.53; Br, 37.3, 37.2.

The pK_a of this bromolycopodinehydrobromide determined in 50% methanol–water medium was 7.30. The infrared spectrum showed absorption in the amine salt region 2500 to 2700 cm.$^{-1}$. The carbonyl band was at 1710 cm.$^{-1}$.

Although this bromination product of lycopodine formed readily and in good yield, attempts to convert it to the free base or to displace the substituted bromine through reactions with silver oxide or potassium acetate, and alkaline or acid hydrolysis, did not lead to any identifiable product.

Bromination of α-Des-dihydrolycopodine

α-Des-dihydrolycopodine (0.50 gm.) was treated with bromine under conditions similar to those for lycopodine. After removal of the solvent under

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vacuum, there remained a quantitative yield of partly crystalline bromohydrobromide salt. Recrystallization from methanol yielded colorless needles, m.p. 275–280° (dec.).

Calc. for $C_{16}H_{26}ONBr.HBr$: C, 46.95; H, 6.66; N, 3.42; Br, 39.2.
Found: C, 46.70, 47.51; H, 7.10, 7.04; N, 3.54, 3.55; Br, 37.6, 38.1.
pK_a (50% methanol–water) = 7.20.

The infrared spectrum in nujol exhibited absorption in the carbonyl region at 1713 cm.$^{-1}$. There was a strong band at 1585 cm.$^{-1}$ attributed to the ionized salt of the secondary amine.

The Reaction of α-Cyanolycopodine with Benzaldehyde

One gram of α-cyanolycopodine and 0.74 gm. of benzaldehyde were dissoved in absolute methanol in a flask equipped with a dropping funnel and reflux condenser. A solution of sodium methoxide in absolute methanol (4 cc. of a solution prepared from 12 gm. of sodium in 150 cc. of methanol) was added to the refluxing solution over a period of 15 min. The reaction mixture was allowed to stand overnight at room temperature and after it had been left for several hours in the refrigerator, crystallization occurred. The first crop of crystals (0.40 gm.) was recrystallized from methanol, to give glistening yellow crystals, m.p. 179.5–180.5°.

The filtrate was concentrated on the steam cone and the residue poured into water to yield an amorphous mass which immediately solidified on warming on the steam cone. The precipitate was collected and dried to yield an additional 0.83 gm. of crude benzylidene derivative. Total yield = 93%.

Calc. for $C_{24}H_{30}ON_2$: C, 79.50; H, 8.35; N, 7.74.
Found: C, 79.52, 79.36; H, 8.34, 8.19; N, 7.80, 7.85.

The infrared spectrum in carbon disulphide contained aromatic absorption bands at 3050 cm.$^{-1}$, 3017 cm.$^{-1}$, and 1617 cm.$^{-1}$; carbonyl absorption at 1690 cm.$^{-1}$; and nitrile absorption at 2215 cm.$^{-1}$. In nujol there was aromatic absorption at 1607 cm.$^{-1}$, carbonyl absorption at 1681 cm.$^{-1}$, and nitrile absorption at 2205 cm.$^{-1}$.

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THE STRUCTURE OF HYOCHOLIC ACID[1]

By P. Ziegler

ABSTRACT

Further evidence for the α-configuration of the hydroxyl groups in hyocholic acid is presented and several related compounds are described.

Two reports (2, 4) have appeared recently describing the isolation and chemistry of hyocholic acid. This compound, derived from hog bile, was characterized as 3α,6α,7α-trihydroxycholanic acid. In order to determine the stereochemical configuration of the hydroxyl groups in ring B, Haslewood (2) partially acetylated ethyl hyocholate to the corresponding 3,6-diacetate (II*b*). Oxidation of II*b* followed by hot alkaline hydrolysis provided a compound of m.p. 211–215°C. and $[\alpha]_D^{23}$ +12.3° (ethanol) to which structure IV was arbitrarily assigned. This finding does not agree with the results of Takeda *et al.* (3) who claimed to have isolated IV, m.p. 183–185°C. and $[\alpha]_D^{15}$ −62.5° (methanol), by very mild saponification of 3α-acetoxy-6α-bromo-7-ketocholanic acid methyl ester. The Japanese authors mentioned that their compound IV yielded the well-known 3α,6α-dihydroxycholanic acid (hyodesoxycholic acid) on reaction with ethanedithiol and subsequent reduction with Raney nickel; however, no experimental evidence for this transformation was cited. They also showed that IV, on being refluxed with methanolic potassium hydroxide, readily isomerized to a product of m.p. 227°C. and $[\alpha]_D^{15}$ +46.4° (methanol) which they characterized as 3α,7-dihydroxy-6-keto-allocholanic acid. Furthermore, this latter compound was the sole material isolated after hot alkaline hydrolysis of the 6-bromo-steroid mentioned before.

Our evidence (4) for the α-configuration of the hydroxyl groups in ring B of hyocholic acid was based on acetonide formation and on optical rotation data. To obtain more rigorous proof, a reaction scheme very similar to that of Haslewood (2) was investigated. We acetylated methyl hyocholate and isolated a crystalline fraction which unfortunately could not be purified chromatographically to a constant melting point. It was therefore decided to forego isolation at this stage, and the entire reaction mixture (crude II*a*) was subsequently oxidized with chromic acid; no crystalline product was obtained. It may be mentioned that Takeda *et al.* (3) also were unable to isolate III in crystalline form. Part of crude III was then saponified under very mild conditions to provide IV, m.p. 180–183°C. and $[\alpha]_D^{25}$ −47.5° (methanol). More drastic alkaline hydrolysis yielded a different product (V), m.p. 234–236°C. and $[\alpha]_D^{25}$ +39.6° (methanol). Both these findings are in accord with the results of the Japanese authors (3). The product isolated by Haslewood (2) and assigned structure IV is probably a mixture of the two isomers IV and V. This can readily be explained by analogy to the ketol rearrangements observed

[1]*Manuscript received June 28, 1956.*
Contribution from the Research and Development Laboratories of Canada Packers Ltd., Toronto, Ont.

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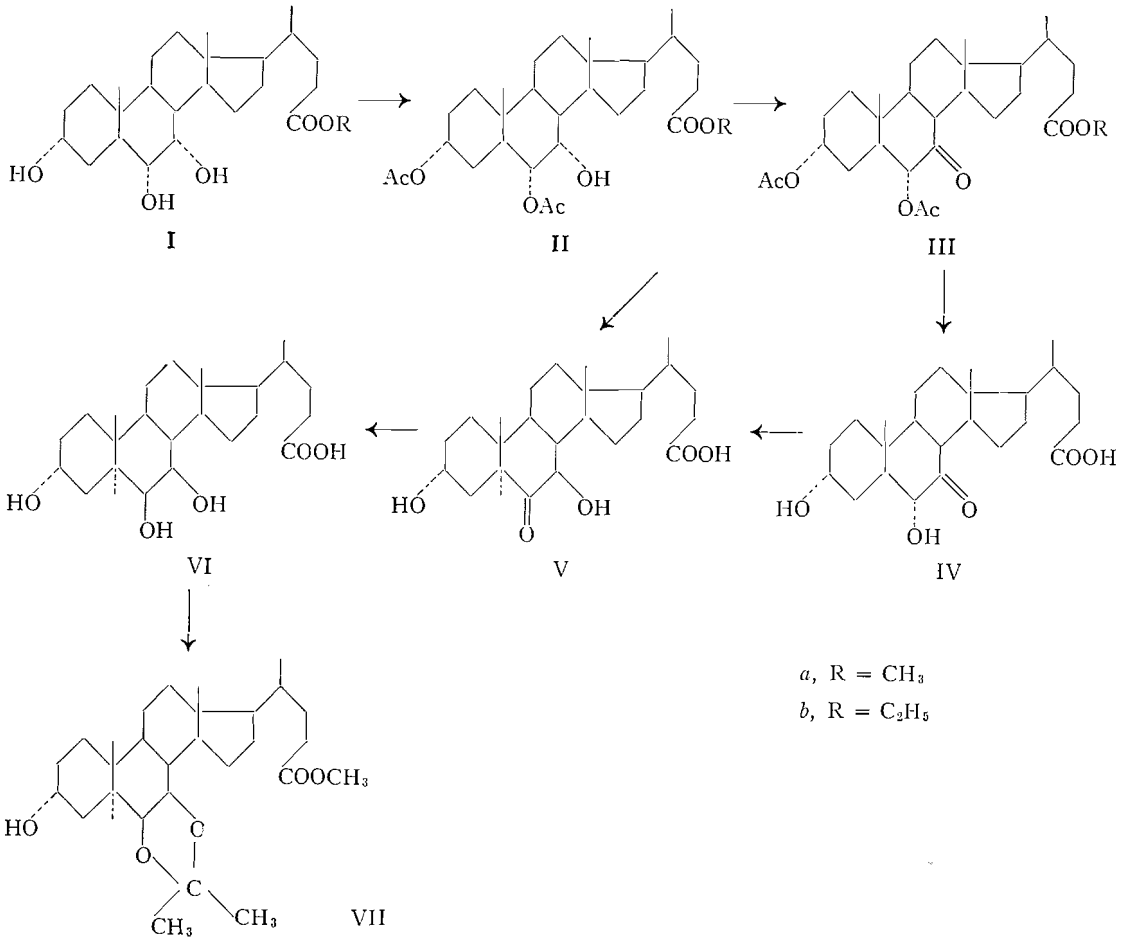

a, R = CH_3
b, R = C_2H_5

in ring C of the steroids. Borgstrom and Gallagher (1) found that 3α,12β-dihydroxy-11-ketocholanic acid, on being refluxed with hot alkali, yielded a mixture from which all four possible isomers were isolated. As expected the two isomers having the hydroxyl group in the more stable equatorial conformation predominated and accounted for 94% of the products. In compound IV, the 6α-hydroxyl group is also equatorial but in contact with hot alkali isomerizes to the intermediate 3α,7β-dihydroxy-6-ketocholanic acid. This compound, in turn, readily isomerizes to the thermodynamically more stable product V in which the ring A/B junction is *trans* and the 7β-hydroxyl group is equatorial.

Reduction of V with sodium borohydride expectedly yielded VI, having the 6β-hydroxyl function in the axial conformation. This compound gave a well-defined, crystalline acetonide on treatment with acetone and *p*-toluenesulphonic acid, which showed that both hydroxyl groups in ring B of VI must have the β-configuration. These data therefore clearly establish the structures of V and VI. The fact that III gave rise to the two isomers, IV or V, depending on the conditions of alkaline hydrolysis, lends further support to the previously assigned stereochemistry of hyocholic acid.

EXPERIMENTAL[2]

3α,6α-Diacetoxy-7-ketocholanic Acid Methyl Ester (IIIa)

Methyl hyocholate (I*a*; 2.75 gm.) was acetylated at 20°C. with pyridine (12 ml.) and acetic anhydride (20 ml.). After 20 hr., the solvents were removed *in vacuo* at 30°C. and the residue was taken up in ether and dilute mineral acid. The solvent extract was washed, dried, and evaporated to provide a gum (3.4 gm.) which crystallized from hexane–ether, giving 770 mgm. of material, m.p. 130°C. This fraction, on recrystallization from the same solvents, gave m.p. 140–155°C. and chromatography on alumina (acid washed) gave crystalline fractions, none of which exhibited sharp melting points. Since isolation of II*a* in pure form could not be achieved, the solid product was recombined with the remaining gum.

The entire residue from the acetylation (crude II*a*; 3.4 gm.) was then dissolved in acetic acid (25 ml.) and water (5 ml.), and the solution was cooled in an ice bath. After dropwise addition of a solution of chromium trioxide (0.5 gm.) in 80% acetic acid (10 ml.), the mixture was kept at 0°C. for two hours. The reaction products were diluted with water containing a small amount of sulphuric acid, extracted with ether, and the solvent extract was washed with dilute sulphuric acid, then with water. Drying over sodium sulphate and evaporation of the ether provided a residue (III*a*; 3.4 gm.)which failed to crystallize.

3α,6α-Dihydroxy-7-ketocholanic Acid (IV)

Crude III*a* (400 mgm.) was dissolved in methanol (10 ml.) and there was then added a solution of potassium hydroxide (150 mgm.) in water (2 ml.). After 40 hr. at 20°C., the pale yellow solution was poured into dilute hydrochloric acid and the mixture was extracted with ether. The extract was washed

[2]*The microanalyses were kindly performed by Mr. E. Thommen, Basel, Switzerland.*

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with water, dried, and evaporated. The residue was dissolved in a small volume of ether and refrigerated to yield 50 mgm. of material, m.p. 177–178°C. Recrystallization from ethyl acetate gave IV, m.p. 180–183°C. and $[\alpha]_D^{25}$ −47.5° (*c*, 0.393, methanol). Analysis: Calc. for $C_{24}H_{38}O_5$: C, 70.90; H, 9.42; O, 19.68. Found: C, 71.20; H, 9.52; O, 19.39. This compound did not give a coloration with alcoholic ferric chloride solution.

3α,7β-Dihydroxy-6-keto-allocholanic Acid (V)

Crude III*a* (270 mgm.) was refluxed for one and a half hours with 4% methanolic potassium hydroxide (10 ml.). Most of the solvent was evaporated *in vacuo*, the residue was acidified and extracted with ether. The solvent extract was washed with water, dried over sodium sulphate, filtered, and evaporated to dryness. The residue crystallized from ether to provide 60 mgm. of material, m.p. 213–215°C. Two recrystallizations from methanol gave pure V, m.p. 234–236°C. and $[\alpha]_D^{25}$ +39.6° (*c*, 0.19, methanol). Analysis: Calc. for $C_{24}H_{38}O_5$: C, 70.90; H, 9.42; O, 19.68. Found: C, 71.08, 70.94; H, 9.43, 9.58; O, 19.65, 19.76.

3α,6β,7β-Trihydroxy-allocholanic Acid (VI)

Compound V (505 mgm.) was suspended in methanol (25 ml.) and there was then added, during a period of three hours, 1.5 gm. of sodium borohydride. The solution was diluted with water, acidified, and the resulting precipitate was filtered off. The solid was dissolved in a mixture of ethyl acetate and methanol, the solution was distilled to remove the methanol, and, on cooling, crystals formed. These were filtered to give 453 mgm. of material, m.p. 253–255°C.; one further recrystallization yielded pure VI, m.p. 256–257°C. and $[\alpha]_D^{25}$ +49.5° (*c*, 0.417, ethanol). Analysis: Calc. for $C_{24}H_{40}O_5$: C, 70.55; H, 9.87; O, 19.58. Found: C, 70.74, 70.58; H, 9.73, 9.97; O, 20.00

The methyl ester of VI, prepared by reaction with ethereal diazomethane, was crystallized from ether–hexane to give m.p. 142–144°C. and $[\alpha]_D^{23}$ +47.9° (*c*, 0.624, ethanol).

Acetonide VII

Compound VI (150 mgm.), after methylation with diazomethane, was dissolved in dry acetone (10 ml.). After addition of *p*-toluenesulphonic acid (30 mgm.), the solution was kept at 20°C. for 15 hr. The acid was then neutralized with sodium bicarbonate, the mixture was poured into water, and the products were extracted with ether. The solvent extract was worked up in the usual manner to yield a residue which crystallized from a mixture of ether and iso-octane. The crystals (139 mgm.), m.p. 115–119°C., were recrystallized from the same solvents to give thin needles of VII, m.p. 118–120°C. and $[\alpha]_D^{25}$ +57.4° (*c*, 0.62, ethanol). Analysis: Calc. for $C_{28}H_{46}O_5$: C, 72.69; H, 10.02; O, 17.29. Found: C, 72.77, 72.51; H, 10.08, 9.94; O, 16.74.

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TOXIC FLUORINE COMPOUNDS

XII. ESTERS OF ω-FLUOROALCOHOLS[1]

By J. E. Millington and F. L. M. Pattison

ABSTRACT

Representative members of the series of ω-fluoroalkyl methanesulphonates, *p*-toluenesulphonates, acetates, and benzoates have been prepared, and some of their chemical, physical, and toxicological properties determined.

The four classes of esters described in this paper were prepared for toxicological studies; by comparison with the results previously reported for the parent ω-fluoroalcohols (22), it was hoped that information could be obtained regarding the hydrolysis *in vivo* of the different ester groupings. The ω-fluoroalkyl sulphonates were also required as intermediates in the synthesis of other ω-fluorinated compounds, notably iodides (21), thiocyanates (15), thiolacetates (15), and sulphonyl chlorides (18), while the ω-fluoroalkyl acetates and benzoates afforded a convenient means of preparing some of the less stable ω-fluoroalcohols, such as 4-fluorobutanol and 5-fluoropentanol.

PREPARATION

The ω-fluoroalkyl methanesulphonates and *p*-toluenesulphonates were prepared either by esterification of the requisite ω-fluoroalcohols (22) with methanesulphonyl or *p*-toluenesulphonyl chloride, or by the metathesis of ω-fluoroalkyl halides (14, 21) with silver methanesulphonate or *p*-toluenesulphonate (7). Yields are summarized in Tables I and II.

ω-Fluoroalkyl acetates were prepared by fluorination of ω-chloroalkyl acetates, which in turn were prepared either by acetylation of the corresponding ω-chloroalcohols or by ring cleavage of cyclic ethers using acetyl chloride (1, 4, 27). Fluorination with potassium fluoride under pressure in an autoclave as originally recommended by Gryszkiewicz-Trochimowski, Sporzynski, and Wnuk (10) was found to be satisfactory, although disproportionation to polymethylene diacetates and formation of unsaturated compounds by loss of hydrogen halides lowered the yields of the ω-fluoroalkyl acetates. Fluorination of 4-chlorobutyl and 5-chloroamyl acetates with potassium fluoride in diethylene glycol resulted in extensive formation of tetrahydrofuran and tetrahydropyran, due to hydrolysis and hydrogen halide elimination in the alkaline medium, with only small amounts of the ω-fluoroalkyl acetates being obtained. Results of these reactions are summarized in Tables III and IV.

The ω-fluoroalkyl acetates were converted to the parent ω-fluoroalcohols by transesterification or by previously described methods (22) (Table V). Because of the relatively poor yields in the fluorination of the ω-chloroalkyl acetates,

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TABLE I

PREPARATION AND PHYSICAL CONSTANTS OF ω-FLUOROALKYL METHANESULPHONATES

Methanesulphonate	Method of preparation[a]	Yield, %	Boiling point		n_D^{25}
			° C.	mm.	
2-Fluoroethyl methanesulphonate	I	31	118–119	12	1.4145
3-Fluoropropyl methanesulphonate	I	37	84	2	1.4183
4-Fluorobutyl methanesulphonate	II[b]	82	89–90	0.5	1.4242
5-Fluoroamyl methanesulphonate	II[c]	90	112	2	1.4290
6-Fluorohexyl methanesulphonate	I	69	130–131	2.5	1.4315

[a]*Method of preparation: I: esterification of ω-fluoroalcohol with methanesulphonyl chloride in the presence of pyridine; II: metathesis of ω-fluoroalkyl halide with silver methanesulphonate.*
[b]*From 4-fluorobutyl iodide.*
[c]*From 5-fluoroamyl bromide.*

TABLE II

PREPARATION AND PHYSICAL CONSTANTS OF ω-FLUOROALKYL *p*-TOLUENESULPHONATES

p-Toluenesulphonate	Method of preparation[a]	Yield, %	Boiling point		n_D^{25}
			° C.	mm.	
2-Fluoroethyl *p*-toluenesulphonate[b,c]	I	80	138.5–140	1	1.5060
3-Fluoropropyl *p*-toluenesulphonate	I	78	160	2	1.5013
4-Fluorobutyl *p*-toluenesulphonate[c]	II	91	151	1	1.4988
5-Fluoroamyl *p*-toluenesulphonate	I	54	163	0.6	1.4970

[a]*Method of preparation: I: esterification of ω-fluoroalcohol with p-toluenesulphonyl chloride in the presence of pyridine; II: metathesis of 4-fluorobutyl iodide with silver p-toluenesulphonate.*
[b]*Childs et al. (3) report b.p. 135–136° at 1 mm.*
[c]*Preparative details have been reported previously (15).*

TABLE III

PREPARATION AND PHYSICAL CONSTANTS OF ω-CHLOROALKYL ACETATES

Acetate	Method of preparation[a]	Yield, %	Boiling point		n_D^{25}
			° C.	mm.	
2-Chloroethyl acetate[b]	I	84.5	140–144	750	1.4220
3-Chloropropyl acetate[c]	I	81.5	61–64	10	1.4273
4-Chlorobutyl acetate[d]	II	80	84–88	15	1.4320
5-Chloroamyl acetate[e]	II	95	96–98	11	1.4363

[a]*Method of preparation: I: acetylation of ω-chloroalcohol; II: cleavage of cyclic ether with acetyl chloride.*
[b]*Suter and Evans (26) report b.p. 145°.*
[c]*Lespieau (17) reports b.p. 62.3° at 10 mm. and* n_D^{21} *1.431.*
[d]*Bennett and Heathcoat (2) report b.p. 87° at 17 mm.*
[e]*Synerholm (27) reports b.p. 104° at 18 mm.*

the over-all yields to ω-fluoroalcohols were unsatisfactory. Accordingly, fluorination of ω-chloroalkyl benzoates was next examined; it was hoped that by thus altering the acid moiety and hence its influence on the reaction, the yields in the replacement of chlorine by fluorine would be increased.

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TABLE IV

PREPARATION AND PHYSICAL CONSTANTS OF ω-FLUOROALKYL ACETATES

Acetate	Method of preparation[a]	Temp., °C.	Time, hr.	Yield, %	Boiling point °C.	Boiling point mm.	n_D^{25}
2-Fluoroethyl acetate[b]	I	150	48	20	115–119	750	
	I	200	48	41.5	116–117.5	740	1.3784
3-Fluoropropyl acetate[c]	I	200	49	38	41–44	11	1.3863
4-Fluorobutyl acetate[d]	I	240	48	66	56–57	12	1.3949
	II	90	16	12.6	66–68	20	
5-Fluoroamyl acetate[e]	I	200	48	6	72–76	14	
	I	250	120	32	70–71	12	1.4017
	II	93	9	29	71–72	12	
By-products isolated from autoclave fluorinations (Method I)							
Ethylene diacetate[f]					79–81	12	1.4175
Trimethylene diacetate[g]					95	13	1.4206
Pentamethylene diacetate[h]					122	12	1.4262
Pent-4-en-l-yl acetate[i]					46–47	12	1.4159

[a] *Method of preparation: I: autoclave fluorination with potassium fluoride and no solvent; II: fluorination at atmospheric pressure with potassium fluoride in ethylene or diethylene glycol.*

[b] *Knunyants et al. (16) report b.p. 115–116° and* n_D^{20} *1.3820.*

[c] *Gryszkiewicz-Trochimowski et al. (10) report b.p. 137–138°.*

[d] *Gryszkiewicz-Trochimowski et al. (10) report b.p. 55.5–56.0° at 11 mm.*

[e] *Pattison et al. (22) report b.p. 71–72.5° at 11 mm.*

[f] *Wurtz (31) reports b.p. 186–187°.*

[g] *Reboul (24) reports b.p. 209–210°.*

[h] *Hamonet (11) reports b.p. 241°.*

[i] *Paul (23) reports b.p. 150–151° and* n_D^{19} *1.4176.*

TABLE V

PREPARATION AND PHYSICAL CONSTANTS OF ω-FLUOROALCOHOLS

Alcohol	Method of preparation[a]	Yield, %	Boiling point °C.	Boiling point mm.	n_D^{25}
3-Fluoropropanol[b]	I	64	34	11	1.3801
4-Fluorobutanol[c]	II	86	52–55	9	1.3945
	III	54.5	63–65	18	1.3948
5-Fluoropentanol[d]	II	87	71–72	12	
	III	76	71–72	11	
	IV	90	66–67	10	1.4050

[a] *Method of preparation: I: transesterification of ω-fluoroalkyl benzoate; II: acid hydrolysis (9, 22) of ω-fluoroalkyl acetate; III: reductive debenzoylation of ω-fluoroalkyl benzoate; IV: transesterification of ω-fluoroalkyl acetate.*

[b] *Hoffmann (14) reports b.p. 127.8° and* n_D^{25} *1.3771.*

[c] *Gryszkiewicz-Trochimowski (9) reports b.p. 52–53° at 11 mm.*

[d] *Pattison et al. (22) report b.p. 70–71° at 11 mm. and* n_D^{25} *1.4057.*

The ω-chloroalkyl benzoates were prepared either by benzoylation of ω-chloroalcohols or by ring cleavage of the appropriate cyclic ethers using benzoyl chloride (27, 28). Fluorination in the autoclave still resulted in disproportionation to polymethylene dibenzoates, but the yields of ω-fluoroalkyl benzoates were good, showing considerable improvement over those of the corresponding ω-fluoroalkyl acetates. Fluorination of 4-chlorobutyl and 5-chloroamyl benzo-

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ates in diethylene glycol proceeded in very low yield; thus, in the fluorination of 4-chlorobutyl benzoate, isolated by-products included tetrahydrofuran, formed by ring closure, and the mono- and *bis*-(4-benzoyloxybutyl) ethers of diethylene glycol ($HO(CH_2)_2O(CH_2)_2O(CH_2)_4OCOC_6H_5$ and $C_6H_5COO(CH_2)_4O(CH_2)_2O(CH_2)_2O(CH_2)_4OCOC_6H_5$), formed by reaction with the solvent. Results of these reactions are summarized in Tables VI and VII.

TABLE VI

PREPARATION AND PHYSICAL CONSTANTS OF ω-CHLOROALKYL BENZOATES

Benzoate	Method of preparation[a]	Yield, %	Boiling point °C.	Boiling point mm.	n_D^{25}
2-Chloroethyl benzoate[b]	I	91	118–119	3	1.5249
	II[c]	35	112	1	
3-Chloropropyl benzoate[d]	I	79	130–131	2.5	1.5222
4-Chlorobutyl benzoate[e]	II	89	142	2	1.5180
5-Chloroamyl benzoate[f]	II	74	127–130	0.9	1.5140

[a] *Method of preparation: I: benzoylation of ω-chloroalcohol; II: cleavage of cyclic ether with benzoyl chloride.*

[b] *Dobryanskii and Sivertsev (6) report b.p. 139–140° at 40 mm. and* n_D^{20} *1.5283.*

[c] *2-Chloroethoxyethyl benzoate,* $ClCH_2CH_2OCH_2CH_2OCOC_6H_5$, *was also isolated in 34% yield, b.p. 130–132° at 1 mm. and* n_D^{25} *1.5186; Cretcher and Pittenger (5) report b.p. 191° at 25 mm.*

[d] *Zaki (32) reports b.p. 155–156° at 15 mm.*

[e] *Synerholm (28) reports b.p. 132–135° at 2.5 mm. and* n_D^{25} *1.5176.*

[f] *Synerholm (27) reports b.p. 141–143° at 2 mm. and* n_D^{20} *1.5169.*

TABLE VII

PREPARATION AND PHYSICAL CONSTANTS OF ω-FLUOROALKYL BENZOATES

Benzoate	Method of preparation[a]	Temp., °C.	Time, hr.	Yield, %	Boiling point °C.	Boiling point mm.	M.p. or n_D^{25}
2-Fluoroethyl benzoate[b]	I	225	48	79	112–114	10	1.5001
3-Fluoropropyl benzoate	I	210	48	77	126–127	10	1.4962
4-Fluorobutyl benzoate	I	220	48	76	142–143	10	1.4940
	II	120	13	14	121	2	1.4932
5-Fluoroamyl benzoate	I	220	48	57	122	1.5	
	II	115	15	19	156–157	11	1.4912
By-products isolated from autoclave fluorinations (Method I)							
Ethylene dibenzoate[c]							70.5–71
Trimethylene dibenzoate[d]							56–57
Tetramethylene dibenzoate[e]							80
Pentamethylene dibenzoate					174	0.001	1.5397
By-products isolated from diethylene glycol fluorinations (Method II)							
Diethylene glycol mono-(4-benzoyloxybutyl) ether					155	2	1.5179
Diethylene glycol *bis*-(4-benzoyloxybutyl) ether					176	0.2	1.5378

[a] *Method of preparation: I: autoclave fluorination with potassium fluoride and no solvent; II: fluorination at atmospheric pressure with potassium fluoride in diethylene glycol.*

[b] *Schrader (25) reports b.p. 105–107° at 12 mm.; Pattison et al. (20) report b.p. 106–108° at 10 mm. and* n_D^{25} *1.4998.*

[c] *Varvoglis (29) reports m.p. 72–73°.*

[d] *Heim and Poe (12) report m.p. 53°.*

[e] *Gol'dfarb and Smorgonskii (8) report m.p. 80–81°.*

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The ω-fluoroalkyl benzoates were converted to ω-fluoroalcohols either by transesterification or by reductive debenzoylation with lithium aluminum hydride. Results are listed in Table V.

From a consideration of this and earlier studies, the following are the recommended procedures for the preparation of the lower ω-fluoroalcohols: 2-fluoroethanol: direct fluorination of 2-chloroethanol (13); 3-fluoropropanol: direct fluorination of 3-chloropropanol (14, 22); 4-fluorobutanol: autoclave fluorination of 4-chlorobutyl acetate followed by acid hydrolysis; 5-fluoropentanol: autoclave fluorination of 5-chloroamyl benzoate followed by reductive debenzoylation. Optimum conditions for the preparation of the higher ω-fluoroalcohols have been described previously (22).

TOXICITY

The toxicities of the ω-fluoroalkyl esters are shown in Table VIII. The most striking feature is the relative lack of toxicity of 2-fluoroethyl methanesulphonate and *p*-toluenesulphonate. Since 2-fluoroethanol has a toxicity of 10 mgm./kgm., the conclusion may be drawn that these sulphonate esters are not readily hydrolyzed *in vivo*. On the other hand, the fact that the higher members follow the usual dichotomous pattern suggests (19) that hydrolysis is occurring, giving rise to the parent ω-fluoroalcohols.

The ω-fluoroalkyl acetates and benzoates conform very closely to the pattern previously described for the ω-fluoroalcohols; moreover, on a molar basis, the LD_{50} figures for these esters are very similar to those for the parent ω-fluoroalcohols, indicating that they are hydrolyzed readily *in vivo*.

TABLE VIII

TOXICITY OF ω-FLUOROALKYL ESTERS

Value of n in $F(CH_2)_nOX$	LD_{50} for mice (intraperitoneal), mgm./kgm.			
	X = SO_2CH_3	X = $SO_2C_6H_4CH_3$	X = $COCH_3$	X = COC_6H_5
2	*ca.* 100	>100	18.6	38
3	>100	>100	77.6	>100
4	1.0	30	0.96	1.7
5	>100	>100	>100	>100
6	35	—	—	—

It has become increasingly apparent in our study of the toxic effects of the ω-fluorine atom that the 2-fluoroethyl compound in any series is considerably less toxic than the higher even members in the same series. This is borne out in the case of ω-fluorinated alcohols, halides, nitriles, thiocyanates, thiolacetates, acids, aldehydes, etc., all of which have been described earlier. The four classes of esters described herein are consistent with this observation, as can be seen from Table VIII. No work has yet been carried out to determine the cause of this anomaly, but it seems reasonable to surmise that the intramolecular electronic influence of the 2-fluorine atom on the other functional groups (with resultant interference with metabolic breakdown) probably outweighs solubility and steric effects.

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TABLE IX

ANALYTICAL DATA FOR NEW COMPOUNDS

Compound	C, %		H, %		S, %	
	Calc.	Found	Calc.	Found	Calc.	Found
$F(CH_2)_2OSO_2CH_3$	25.35	25.48	4.93	4.99		
$F(CH_2)_3OSO_2CH_3$	30.76	30.71	5.76	5.73		
$F(CH_2)_4OSO_2CH_3$	35.28	35.52	6.51	6.81	18.84	18.50
$F(CH_2)_5OSO_2CH_3$	39.11	39.25	7.11	7.03	17.41	17.29
$F(CH_2)_6OSO_2CH_3$	42.41	42.32	7.62	7.46	16.17	16.03
$F(CH_2)_3OSO_2C_6H_4CH_3$	51.71	51.93	5.64	5.48		
$F(CH_2)_5OSO_2C_6H_4CH_3$	55.36	55.48	6.58	6.44		
$F(CH_2)_3OCOC_6H_5$	65.97	66.10	6.08	6.00		
$F(CH_2)_4OCOC_6H_5$	67.35	67.40	6.63	6.63		
$F(CH_2)_5OCOC_6H_5$	68.60	68.45	7.14	7.44		
$C_6H_5COO(CH_2)_5OCOC_6H_5$	73.05	73.29	6.45	6.39		
$HO(CH_2)_2O(CH_2)_2O(CH_2)_4OCOC_6H_5$	63.83	63.66	7.80	7.72		
$[C_6H_5COO(CH_2)_4O(CH_2)_2]_2O$	68.10	68.32	7.47	7.35		

EXPERIMENTAL[2,3]

Preparation of ω-Fluoroalkyl Methanesulphonates and p-Toluenesulphonates

The following syntheses are representative of the methods employed for the preparation of ω-fluoroalkyl methanesulphonates and *p*-toluenesulphonates.

Method I: the Reaction of a Fluoroalcohol with a Sulphonyl Chloride

3-Fluoropropyl p-toluenesulphonate.—A mixture of *p*-toluenesulphonyl chloride (30.5 gm., 0.16 mole) and pyridine (40 gm.) was stirred at −2°, and 3-fluoropropanol (14) (12.5 gm., 0.16 mole) was added dropwise over two hours. Stirring was continued for a further two hours. The reaction mixture was diluted with water and 6 *N* hydrochloric acid until there was no pyridine odor, and then extracted with ether. The combined extracts were washed successively with water, aqueous sodium carbonate, and water again, and dried over anhydrous sodium sulphate. After removal of the ether, fractionation of the residue yielded 29 gm. (78%) of 3-fluoropropyl *p*-toluenesulphonate.

Method II: the Reaction of a Fluoroalkyl Halide with the Silver Salt of a Sulphonic Acid

5-Fluoroamyl methanesulphonate.—A mixture of 5-fluoroamyl bromide (21) (12.0 gm., 0.07 mole), silver methanesulphonate (14.3 gm., 0.07 mole), and acetonitrile (50 ml.) was heated on a steam bath for one hour. Silver bromide was removed from the cooled mixture by filtration, and the acetonitrile was distilled Fractionation of the residue yielded 5-fluoroamyl methanesulphonate (11.7 gm., 90%).

Preparation of ω-Chloroalkyl Acetates

The following are representative examples of the procedures employed in the preparation of ω-chloroalkyl acetates.

[2]*Analysis results are shown in Table IX.*

[3]*Physical constants are shown in the appropriate tables. Several of the compounds have been described in the literature; their constants are listed herein as criteria of purity and to provide some previously unreported refractive indices.*

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Method I: the Reaction of an Alcohol with Acetyl Chloride

3-Chloropropyl acetate.—A mixture of 3-chloropropanol (118.2 gm., 1.25 moles) and acetyl chloride (100 gm., 1.27 moles) was heated on a water bath (60°) for one hour. It was cooled, washed successively with water and aqueous sodium carbonate, and transferred to a flask fitted for distillation. Ethylene chloride (50 ml.) was added and the water – ethylene chloride azeotrope distilled. The residue on fractionation through a 50 cm. Vigreux column gave 3-chloropropyl acetate (139 gm., 81.5%).

Method II: the Reaction of a Cyclic Ether with Acetyl Chloride

5-Chloroamyl acetate.—Acetyl chloride (110 gm., 1.40 moles) was added with constant stirring to an ice-cooled mixture of redistilled tetrahydropyran (107.5 gm., 1.25 moles) and freshly fused and ground zinc chloride (2.7 gm.). When the addition was complete, the mixture was heated on a steam bath for five hours and then fractionated to give 5-chloroamyl acetate (195 gm., 95%).

Preparation of ω-Fluoroalkyl Acetates

The ω-fluoroalkyl acetates were prepared by one or both of the procedures outlined below.

Method I: Autoclave Method, No Solvent

5-Fluoroamyl acetate.—A mixture of 5-chloroamyl acetate (335 gm., 2.02 moles) and anhydrous potassium fluoride (232 gm., 4.0 moles) was heated in a stainless steel autoclave at 250° for 120 hr. After the autoclave had cooled, the mixture was diluted with water and the layers were separated. The aqueous layer was extracted with ether. The organic layer and extracts were combined, washed with water and aqueous sodium carbonate, and then dried. The ether was distilled, and the residue on fractionation through a modified Podbielniak column gave pent-4-en-1-yl acetate (27.2 gm.), 5-fluoroamyl acetate (95.6 gm., 32%), and pentamethylene diacetate (47.7 gm.).

Method II: Atmospheric Pressure, Diethylene Glycol as Solvent

5-Fluoroamyl acetate.—A mixture of 5-chloroamyl acetate (46 gm., 0.28 mole), anhydrous potassium fluoride (48 gm., 0.83 mole), and diethylene glycol (250 gm.) was heated with constant stirring at 93° for nine hours. Earlier experiments had shown that higher temperatures resulted in lower yields of fluoro ester, and that the use of potassium iodide as a promoter did not increase the yield. The mixture was distilled through a 20 cm. Vigreux column first at atmospheric pressure, giving tetrahydropyran (4.6 gm.), and then under reduced pressure up to the boiling point of diethylene glycol. This material was dissolved in ether, dried over anhydrous sodium sulphate, and fractionated through a 30 cm. Vigreux column, giving 5-fluoroamyl acetate (12 gm., 29%).

Preparation of ω-Chloroalkyl Benzoates

The ω-chloroalkyl benzoates were prepared by procedures analogous to those employed for the ω-chloroalkyl acetates.

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Method I: the Reaction of an Alcohol with Benzoyl Chloride

3-Chloropropyl benzoate.—3-Chloropropanol (100 gm., 1.06 moles) was added with constant stirring to an ice-cooled mixture of benzoyl chloride (150 gm., 1.06 moles), pyridine (85 gm., 1.07 moles), and anhydrous ether (100 ml.). When the addition was complete, the mixture was stirred at room temperature for 2.5 hr., diluted with water, and extracted with ether. The combined extracts were washed successively with water, aqueous sodium carbonate, and water again, and dried over anhydrous calcium chloride. The ether was removed on the water bath and the residue on fractionation through a 25 cm. Vigreux column gave 3-chloropropyl benzoate (164.6 gm., 79%).

Method II: the Reaction of a Cyclic Ether with Benzoyl Chloride

2-Chloroethyl benzoate.—Benzoyl chloride (70.25 gm., 0.5 mole) was added over 1.8 hr. to a well-stirred mixture of ethylene oxide (44 gm., 1.0 mole) and freshly fused zinc chloride (3 gm.), cooled in an ice–salt bath. The mixture was stirred for a further two hours, and then heated on a steam bath for 30 min. The mixture was cooled, diluted with water, and extracted with ether. The extracts were washed with water and dried over anhydrous calcium chloride. The ether was distilled and fractionation of the residue gave 2-chloroethyl benzoate (32.5 gm., 35%), 2-chloroethoxyethyl benzoate (39.1 gm., 34%), and ethylene dibenzoate (16 gm.).

Preparation of ω-Fluoroalkyl Benzoates

Below are outlined the procedures which were employed for the preparation of ω-fluoroalkyl benzoates.

Method I: Autoclave Method, No Solvent

2-Fluoroethyl benzoate.—A mixture of 2-chloroethyl benzoate (167 gm., 0.91 mole) and anhydrous potassium fluoride (116 gm., 2.0 moles) was heated in a stainless steel autoclave with mechanical stirring at 225° for 48 hr. After the autoclave had cooled, the mixture was diluted with water and extracted with ether. The combined extracts were washed with water and dried over anhydrous calcium chloride. Removal of the ether and fractionation of the product gave 2-fluoroethyl benzoate (86 gm.), unchanged 2-chloroethyl benzoate (48 gm.), and ethylene dibenzoate (4 gm.). This represents a yield of 79% based on reacted starting material.

Method II: Atmospheric Pressure, Diethylene Glycol as Solvent

4-Fluorobutyl benzoate.—A mixture of 4-chlorobutyl benzoate (106.3 gm., 0.5 mole), anhydrous potassium fluoride (116 gm., 2.0 moles), and diethylene glycol (200 gm.) was heated at 120° with constant stirring for 13 hr. The mixture was cooled, diluted with water, and extracted with ether. The extracts were washed with water and dried over anhydrous magnesium sulphate. The ether was distilled and the residue fractionated to give a small forerun of 4-fluorobutanol, and then 4-fluorobutyl benzoate (12 gm., 14%), 4-chlorobutyl benzoate (16.5 gm.), diethylene glycol mono-(4-benzoyloxybutyl) ether (40.5 gm.), and diethylene glycol *bis*-(4-benzoyloxybutyl) ether (6 gm.).

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Preparation of ω-Fluoroalcohols

The ω-fluoroalcohols were prepared by the procedures outlined below.

Method I: Transesterification of ω-Fluoroalkyl Benzoate

3-Fluoropropanol.—A mixture of 3-fluoropropyl benzoate (18.2 gm., 0.1 mole), *p*-toluenesulphonic acid (0.5 gm.), and absolute methanol (100 ml.) was heated under reflux for 12 hr. Fractionation of the product gave 3-fluoropropanol (5.0 gm., 64%).

Method II: Acid Hydrolysis of ω-Fluoroalkyl Acetate

4-Fluorobutanol.—A mixture of 4-fluorobutyl acetate (172 gm., 1.28 moles) and 5% aqueous sulphuric acid (600 ml.) was heated under reflux until homogeneous (*ca.* 30 min.). The mixture was cooled, saturated with solid sodium bicarbonate, and extracted with ether. The extracts were dried over anhydrous sodium sulphate, the ether was removed, and the residue was fractionated to give 4-fluorobutanol (101 gm., 86%).

Method III: Reductive Debenzoylation of ω-Fluoroalkyl Benzoate

5-Fluoropentanol.—A solution of 5-fluoroamyl benzoate (13.3 gm., 0.064 mole) in anhydrous ether (125 ml.) was added with constant stirring to a suspension of lithium aluminum hydride (3.2 gm., 0.083 mole) in anhydrous ether (200 ml.) at such a rate that the ether boiled gently under reflux. When the addition was complete, the mixture was stirred for a further 30 min. Water was added to decompose the excess hydride, the reaction flask being cooled in an ice bath. The complex was hydrolyzed with 10% aqueous sulphuric acid and the ethereal layer was separated. The aqueous layer was extracted with ether and the combined extracts were dried over anhydrous potassium carbonate. The ether was removed on the water bath and the residue on fractionation gave 5-fluoropentanol (5.1 gm., 76%).

Method IV: Transesterification of ω-Fluoroalkyl Acetate

5-Fluoropentanol.—A mixture of 5-fluoroamyl acetate (44.4 gm., 0.30 mole), *p*-toluenesulphonic acid (0.5 gm.), and absolute methanol (150 ml.) was heated under reflux for 19.5 hr. Fractionation of the product gave 5-fluoropentanol (28.5 gm., 90%).

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LIGHT ABSORPTION STUDIES

PART VI. THE EFFECTIVE INTERFERENCE VALUES OF NON-BONDED ATOMS IN SOLUTION. PART I. SOME PRELIMINARY OBSERVATIONS[1]

By W. F. Forbes and W. A. Mueller

ABSTRACT

The application of light absorption data to determine minimum interference radii of various atoms in solution is examined. Three separate methods are suggested and the relation between potential energy and interatomic distance of two non-bonded atoms is discussed. The values obtained in neutral solution are as follows: H, 0.95±0.1 Å; O (in C=O), 1.0±0.15 Å; and CH_3, 1.7±0.2 Å.

INTRODUCTION

The size of the hydrogen and other atoms in neutral solution is important for at least two reasons. First, it enables us to construct molecular models with correct interplanar angles. Secondly, values for a fixed set of conditions will aid the study of the relation of these interference values with temperature, concentration, pH, and dielectric constant of the solvent.

Yet the assignment of interference radii to various atoms in solution has been a subject of considerable discussion. Early attempts were made by Latimer and Rodebush (26), and Adams and Yuan (2) developed values based on substituted diphenyls. More recently Crombie (12) has proposed a value for the hydrogen interference radius of 0.75 Å, and Braude and Sondheimer (8) have used a value of 0.60 Å. The choice of these values rests on the belief that van der Waal's radii are too large a measure of steric hindrance in solution, and covalent radii too small. Covalent radii would not account for the large number of observed steric effects in solution (for example, those affecting the B-band of ultraviolet light absorption data (cf. Parts I, II, and III (16, 17, 20) of this series); van der Waal's radii cannot be used without modification since under the conditions discussed (that is, in neutral solution at room temperature) there may be some energy available inherent in these particular conditions. For example, a solution energy of say 5 kcal./mole may permit ready interaction of two atoms to within a distance which corresponds to a smaller interaction energy, say 1 kcal./mole.

A good illustration of this problem is provided by the diphenyl molecule. Electron diffraction measurements (4, 25), which give data about the isolated molecule, show diphenyl to be non-planar; the angle between the two rings has been reported as large as 45±10°, and the 1–1′ bond distance as 1.54 ±0.03 Å (25), corresponding to a carbon–carbon single-bond with little double-bond character. X-ray methods, on the other hand, show diphenyl to be planar in the crystalline state; with a 1–1′ bond distance of 1.48 Å, indicating appreciable double-bond character (14). This must be ascribed to forces prevailing in the crystalline state, sufficiently strong to overcome the interaction energies

[1]*Manuscript received May 23, 1956.*
Contribution from Memorial University of Newfoundland, St. John's, Newfoundland.

of the *ortho*-hydrogen atoms. (We are assuming that in the gaseous state there is a certain amount of steric hindrance because of mutual interaction of the *ortho*-hydrogen atoms. This seems reasonable, since it is difficult to postulate any other factor which would oppose the tendency of the resonance energy to keep the molecule planar.)

The particular problem for diphenyl is whether the molecule is planar or non-planar *in solution*. If it is planar, the effective interference value of the hydrogen atoms must be less than 0.90 Å; this is the value obtained for the two (assumed spherical) hydrogen atoms in a planar molecule just touching, using the accepted values for carbon–carbon and carbon–hydrogen distances and bond angles (14, 27). If the diphenyl molecule can be shown to be non-planar, the effective interference value of the hydrogen atoms must similarly be greater than 0.90 Å.

The more general problem may then be attempted thus: Having obtained from this and other examples a number of maximum and minimum values for the hydrogen and other atoms, these values can then be used to calculate interplanar angles, which in turn may be checked against other available data. The assumption is that the value for the effective interference radius of hydrogen will be similar for most molecules. This is not necessarily true and will be referred to again later; however, it will serve as a first approximation.

INTERFERENCE RADII FROM STERIC EFFECTS IN THE B-BANDS OF ABSORPTION SPECTRA

Steric effects in the B-bands of absorption spectra can be divided into three types, depending on the magnitude of the steric interaction (8, 16). The smallest amount of steric interaction detectable by this method gives rise to a steric effect of type I, namely a decrease of transition probability unaccompanied by a change in location of maximal absorption. The theoretical interpretation of this steric effect has recently been discussed (8, 18).

Since steric effects of type I have been ascribed to interaction between non-bonded atoms, we can use examples where steric effects of this type occur to calculate minimum interference values of non-bonded atoms which cause the steric interaction. Suitable examples of type I steric hindrance consequently represent the minimum steric interaction which may be detected directly from absorption spectra. Examples will be suitable if they indicate a steric effect beyond reasonable doubt. On the other hand the steric effect should not be too pronounced because a large steric effect represents a large interplanar angle; thus the minimum value based on a planar molecule will be considerably less than the actual interference value. This follows because the interference value is based on the assumption that the non-bonded atoms just touch; that is, the molecule is near-planar or only just planar. Further, bending effects have also been neglected which emphasize that values obtained represent minimum values. The two examples discussed are acetophenone and 2-methyl-benzaldehyde.

Acetophenone absorbs maximally at 240 mμ, ϵ = 12,500, while benzaldehyde under identical conditions absorbs maximally at 244 mμ, ϵ = 13,000 (16).

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Since substitution of a $COCH_3$- for a CHO-group does not normally give a hypsochromic shift—for example CH_2=CH.CHO and CH_2=CH.$COCH_3$ absorb maximally at 206 (ϵ = 10,500) and 207.5 mμ (ϵ = 10,000) respectively under identical conditions (Bowden, Heilbron, Jones, and Weedon (6) report a maximal absorption of 210 mμ for methylvinyl ketone)—we may assume that acetophenone is sterically hindered with respect to benzaldehyde.* By means of a scale diagram of acetophenone we can thus obtain a minimum value for the effective interference radius of the hydrogen atom. This is illustrated in Fig. 1. It is necessary to consider the sterically less favorable conformation

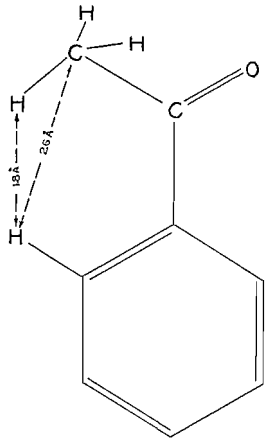

FIG. 1. Scale diagram of the less favorable planar configuration of acetophenone.

because conceivably the more favorable conformation may not contribute to the observed effect (cf. 18). The hydrogen value obtained by this method is 0.93 Å, in good agreement with the value obtained for a diphenyl molecule which is just planar. We can also use Fig. 1 to obtain directly a value for the effective interference radius of a methyl-group. The value thus obtained is 1.7 Å, identical with the value used by Braude and Sondheimer (8).

Concerning the *actual* interplanar angle of acetophenone, it is difficult to ascertain this with certainty, since it has been shown that small interplanar angles (up to 20°) will not affect the resonance interaction to any great extent (13, 22, 28). For acetophenone the interplanar angle is probably small; 4-methylacetophenone has been assumed planar (18) and although the absence of the methyl-group presumably lessens the coplanarity of the molecule (see below), the difference in interplanar angle is unlikely to be very appreciable.

A similar approach may be used for 2-methylbenzaldehyde which absorbs maximally at 251 mμ, ϵ = 13,000, while 4-methylbenzaldehyde under similar conditions absorbs maximally at 251 mμ, ϵ = 15,000 (8). If we then conclude that the spectrum of 2-methylbenzaldehyde exhibits a typical type I steric effect, and base our calculations on the sterically less favorable conformation, the scale diagram gives an interference value for the oxygen atom of 0.62 Å,

We are indebted to Dr. J. S. Fawcett for suggesting this example to us.

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or 0.85 Å, depending on whether the value H = 0.9 Å or CH_3 = 1.7Å is used. This value is almost certainly low because a planar molecule has been assumed whereas an estimate of interplanar angles (cf. 18) suggests an interplanar angle of 31° for the *s-cis* form of 2-methylbenzaldehyde. This would correspond to the much more likely interference radius of 1.1 Å for the carbonyl oxygen.

A further check may be obtained from the estimate of 50° for the interplanar angle of the *s-cis* form of 2-methylacetophenone. This leads to a value of 1.5 Å for the interference radius of the methyl-group.

Finally, in this section evidence ascribed to the "buttressing effect" may be used to confirm the proposed values. In molecules where both *ortho*- and *meta*-positions adjacent to an auxochrome are substituted, the steric effect is frequently enhanced relative to the *ortho*-substituted compound. Light absorption data indicate this buttressing effect to be due to steric rather than electronic causes (7, 16), an observation which is confirmed by the racemization rates of substituted diphenyls (1).

Using light absorption data to obtain interference radii, 2,3,5,6-tetramethyl- and 2,3,4,5,6-pentamethyl-acetophenones both exhibit distinct buttressing effects compared to the corresponding *meta*-unsubstituted reference compounds. The value thus obtained for the interference radius of the methyl-group is 1.47 Å, but this low value is not surprising since the steric effect as observed is quite appreciable (see 16). Consequently calculations based on the minimum detectable effect would lead to a larger value for the interference radius. This is in fact obtained, by considering interaction between a hydrogen atom and an adjacent methyl-group in the *meta*-position. The value for the interference radius of the methyl-group then obtained is 1.8 Å, assuming an interference radius of 0.9 Å for the hydrogen atom in a planar molecule. Spectral data actually indicate—since for example 3,3′-dimethyldiphenyl absorbs maximally at 255 mμ, ϵ = 16,500, while diphenyl itself absorbs maximally at 249 mμ, ϵ = 17,000 (7)—that a slight "buttressing-effect type" interaction occurs under these conditions; hence the value of 1.8 Å may provisionally be taken as another value obtained for the interference radius of the methyl-group.

THE NON-PLANARITY OF THE DIPHENYL MOLECULE AS EVIDENCED FROM TEMPERATURE EFFECTS ON THE SPECTRUM OF DIPHENYL

The ultraviolet absorption spectrum of diphenyl has been determined in the vapor phase between 170° and 520° C. (3). The data are recorded in Table I. Between 170° and 520° a bathochromic shift occurs accompanied by decreased absorption intensity at maximal wavelength. Using the schematic representations which have been found satisfactory in correlating various steric effects (18), it may be shown that a planar diphenyl molecule cannot account for the observed effect (i.e. a bathochromic shift), while a non-planar diphenyl molecule can account for the data (see Fig. 2).

In a planar diphenyl molecule (see Fig. 2(*a*)) increase of temperature (from T_1 to T_2 and to T_3) gives rise to progressive hypsochromic shifts as the mean transition energies become larger. Absorption associated with certain vibra-

TABLE I

LIGHT ABSORPTION CONSTANTS OF DIPHENYL (B-BANDS) IN THE VAPOR PHASE (3)

	(20° in hexane)	170°	260°	360°	520°
$\lambda_{max}(m\mu)$	$\simeq 245$	238.1	———	→	239.5
ϵ_{max}	16,430	12,050	10,900	9900	9400

tional levels (for instance, at temperature T_3) will not necessarily always lead to actual transitions, but the increase of temperature will make transitions involving greater energy changes more probable, and thus further increase the mean transition energy. The absorption intensity may be expected at first to remain approximately constant as the temperature increases from T_1 to T_2, and then to decrease as the temperature approaches T_3, because potential electronic excitations from higher vibrational levels no longer lead to actual transitions.

In non-planar diphenyl molecules, as the temperature increases from T_1 to T_2 and T_3, the mean transition energy can become smaller and a *bathochromic* shift may be observed. For the extreme example illustrated in Fig. 2(*b*), the absorption intensity will remain approximately constant over the range T_1 to T_3.

A diphenyl molecule with an interplanar angle intermediate to those illustrated in Figs. 2(*a*) and (*b*), when the temperature is increased, may exhibit a hypsochromic shift followed by a bathochromic shift, or vice versa. However, a bathochromic shift indicates non-planarity, and the observed bathochromic shift therefore confirms the non-planarity of the diphenyl molecule in the vapor phase.

If we now assume that addition of hexane for the value at 20° will not appreciably affect the energy relationships of the ground state, we would have evidence concerning the non-planarity of the diphenyl molecule in solution. This supposition seems reasonable since *n*-hexane is an inert solvent and because dilution experiments (see Table II) indicate that association under these conditions is negligible.

TABLE II

THE ABSORPTION OF DIPHENYL AT DIFFERENT CONCENTRATIONS IN CYCLOHEXANE AND ABSOLUTE ETHANOL (21)

Solvent	Cell length (cm.)	Concentration (moles/l.)	λ_{max} ($m\mu$)	ϵ_{max}
Cyclohexane	0.1	2.6×10^{-4}	247	16,200
Cyclohexane	4	6.5×10^{-6}	246	15,600
Ethanol	0.1	2.8×10^{-4}	247	17,300
Ethanol	4	7.1×10^{-6}	246	17,300

Further, diphenyl absorbs in different solvents at approximately the same wavelength and intensity, which suggests the absence of the equivalent of

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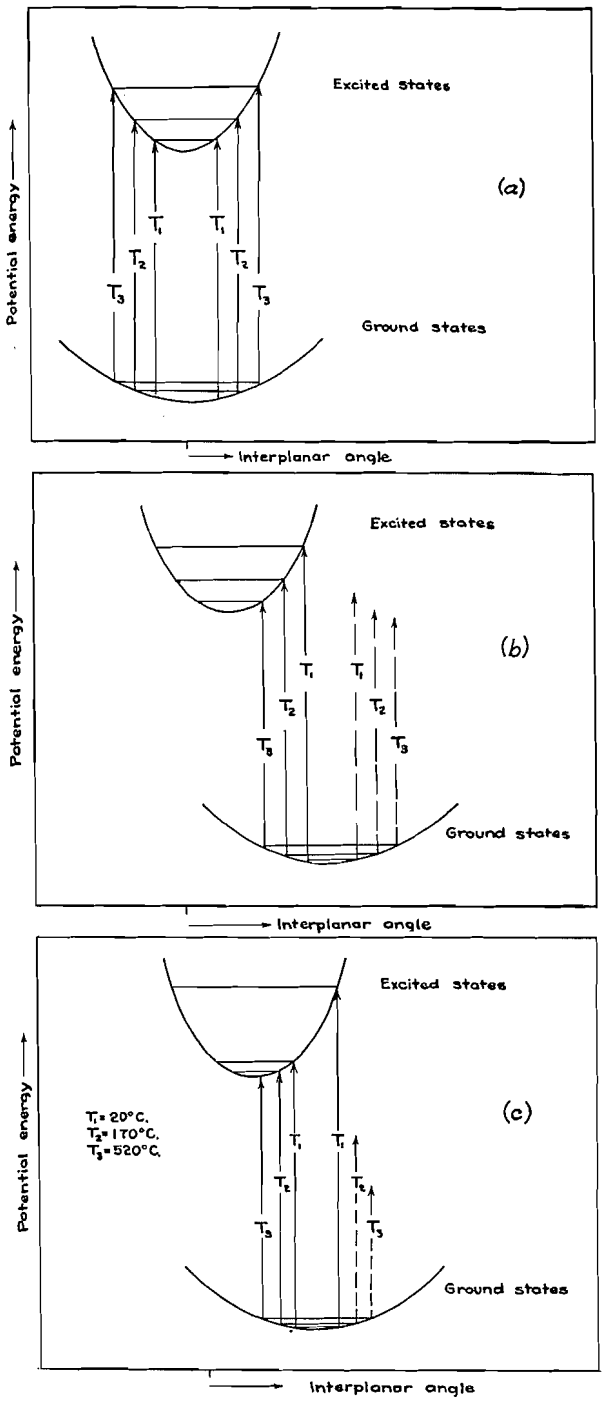

FIG. 2. Schematic representation of electronic transitions between ground and excited states in diphenyl; with (*a*) interplanar angle assumed to be zero, (*b*) interplanar angle assumed to be large, (*c*) actual interplanar angle.

lattice forces (as in the solid state) to overcome the steric interaction between the *ortho*-hydrogens. If such forces were present in the liquid state one would expect these forces to vary with the solvent and concentration. Hence the absence of appreciable solute–solvent interaction (as is indicated from the data reported in Table II) favors the view that the energy relationships in the solution phase are similar to those obtained in the gas phase, and is consequently opposed to the view that the energy relationships in the solution phase are necessarily intermediate between those of the gas and solid phases.

The very much higher absorption intensity at room temperature may readily be explained by an interplanar angle as illustrated in Fig. 2(*c*). The latter also summarizes our hypotheses concerning the electronic transitions of diphenyl at various temperatures.

The effect of temperature on the absorption spectra of various other compounds has been reported to give rise to different effects (5, 23, 24, 30); further work to correlate these effects with interplanar angles and solvent effects is in progress and will be the subject of a separate communication.

INTERFERENCE RADII AS DEDUCED FROM THE EFFECTS OF *PARA*-SUBSTITUENTS

This method arises as a possible development of a suggestion made by Braude and Sondheimer (8), who noted that a *para*-methyl substituent may either enhance or reduce the steric effect of an *ortho*-substituent. It was found that in 2,4,6-trimethylbenzaldehyde a *para*-methyl group reduces the *ortho*-effect, whereas in 2,4,6-trimethylacetophenone it enhances it. The suggestion of Braude and Sondheimer (8) was that the additional conjugation reduces the non-planarity of the system *if* steric hindrance is weak; if, however, the steric hindrance is large, the additional conjugation merely enhances the congestion at the acetyl group.

This follows since introduction of a *para*-methyl substituent increases the resonance energy and because the interplanar angle is determined essentially by an equilibrium between resonance and interaction energies. Hence a gain of resonance energy greater than the increase of steric interaction energy, caused by the bond shortening, will lead to a decreased interplanar angle. Conversely, if the increase in resonance energy is less than the gain in steric interaction energy, an increased interplanar angle will result.

The method therefore has distinct possibilities to determine, firstly, the onset of steric interaction (and hence the effective interference radii), and more generally the amount of steric interaction present, provided the gain in resonance energy is known. However, before it is possible to detect the onset of small decreases (due to steric interaction) in the over-all stabilization produced by the increased resonance energy, it is necessary to consider some other factors which may also affect the changes in intensity and wavelength of maximal absorption. These may be formulated as follows:

(i) The conjugating effect of a *para*-methyl group will vary depending on the amount of conjugation already present. For example, the effect would be expected to be larger in a medium such as sulphuric acid, where the stability

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of dipolar contributing forms would be enhanced by the ionizing properties of the solvent. Similarly, if the auxochrome has a large negative *mesomeric* effect (for example, —$COCH_3$ or —NO_2), the change due to the *para*-methyl group would be expected to be greater than if the auxochrome has a small or a positive *mesomeric* effect (for example, —CH_3 or —NH_2; cf. also (19)).

(ii) The *para*-methyl group may change the amount of association between molecules. Association has been shown to vary when the molecular structure is modified even slightly (21) and this may consequently affect the wavelength and intensity changes.

(iii) *para*-Methyl substituents may increase the force constant of the bond linking the two planar entities. This will lead to less "shallow" potential energy curves throughout, but the change will be more pronounced in the excited than in the ground states.

We may now attempt to interpret the data recorded in Table III. It is noted that a number of compounds on *para*-methyl substitution exhibit batho-

TABLE III

CHANGES OBSERVED ON INTRODUCING A *para*-METHYL GROUP IN A NUMBER OF AROMATIC SYSTEMS

Compound	Without *para*-methyl		With *para*-methyl			
	$\lambda_{max}(m\mu)$	$\epsilon_{max}(\epsilon_0)$	$\lambda_{max}(m\mu)$	ϵ_{max}	$\Delta\lambda$	ϵ/ϵ_0
Benzaldehyde[1]	242	14,000	251	15,000	9	1.07
Acetophenone[2]	243	13,200	252	15,100	9	1.14
Benzoic acid[3]	227	11,000	236	14,000	9	1.3
Toluene[4]	207.5	7,000	211	7,200	3.5	1.0
Nitrobenzene (in *iso*octane)[5]	252	8,600	264	10,300	12	1.2
Benzaldehyde (in H_2SO_4)[6]	293	21,000	309	23,000	16	1.1
Acetophenone (in H_2SO_4)[5]	295	28,000	311.3	30,000	16.3	1.1
Acetanilide[3]	242	14,500	245	15,000	3	1.0
Diphenyl[4]	247	17,300	250	17,700	3	1.0
2,6-Dimethylbenzaldehyde[1]	251	12,500	264	14,500	13	1.2
2-Methylacetophenone[2]	242	8,700	251	14,100	9	1.6
2,6-Dimethylacetophenone[2]	251	5,600	242	3,600	−9	0.6

[1]*Reference 8; in hexane.*
[2]*Reference 8.*
[3]*Reference 20.*
[4]*This paper.*
[5]*Reference 11.*
[6]*Reference 19.*

chromic shifts of about 9 mμ and an ϵ/ϵ_0 ratio of about 1.1. For compounds where the negative *mesomeric* effect of the auxochrome is large (for example, nitrobenzene) or for spectra in sulphuric acid solution, the wavelength change is much greater.

The slight change in the ϵ/ϵ_0 ratio from acetophenone to benzaldehyde may represent the known steric hindrance exhibited by the former; however, the data are insufficiently conclusive at this stage to permit a decision. Furthermore, minor steric interactions appear to give rise to a variety of effects. For example, steric interactions may give rise to an abnormally small positive wavelength shift, as from diphenyl to 4-methyldiphenyl; or it may lead to an abnormally large positive wavelength shift, as from 2,6-dimethyl- to 2,4,6-trimethyl-benzaldehyde; or again it may result in considerably in-

creased intensity of absorption, for example from 2-methyl- to 2,4-dimethyl-acetophenone (see Table III). Detailed discussion of these phenomena also will therefore be deferred for the present.

Another application of this method is that it may be used to calculate directly interaction energies from known interatomic distances between sterically interacting atoms. Thus, if on introducing a *para*-methyl group a negative wavelength change is observed, when a positive shift is normally obtained, then this change in wavelength will correspond to the steric interaction energy increase. For instance, we may assume that the gain of resonance energy on introducing a *para*-methyl substituent in both 2-methyl- and 2,6-dimethyl-acetophenone is approximately 9 mμ; since 2,4,6-trimethylacetophenone actually exhibits a hypsochromic shift of 9 mμ, the steric interaction will be equivalent to a wavelength change of about 18 mμ. This corresponds to 8 kcal./mole, and since we estimated the interplanar angle of 2,4,6-trimethyl-acetophenone to be 63° (which in turn corresponds to a distance of 3.2 Å between the two adjoining methyl-groups), we now obtain a value of 8 kcal./mole for two methyl-groups 3.2 Å apart.

This then represents one aspect, perhaps the most promising of the method, though evidently more subtle applications may become possible at a later stage.

CONCLUSIONS

The minimum interference values thus obtained are: hydrogen, 0.93, 0.90 Å; oxygen (in C=O), (0.62, 0.85), 1.1 Å; and methyl-group, 1.7, 1.5, (1.47), 1.8, 1.7 Å. Although the variation obtained is not too large (omitting the more doubtful bracketed values), it must be remembered that the effective interference radius of an atom will not be constant under different conditions. This variation may depend on a number of factors, such as:

(*a*) the type of covalent bond involved;

(*b*) the nature of the opposing (interfering) partner;

(*c*) the direction of maximum interference relative to the direction of its valency;

(*d*) the temperature;

(*e*) the degree of association with solvent molecules;

(*f*) the pH of the solvent;

(*g*) the dielectric constant of the solvent.

In the present communication only similar benzenoid compounds are discussed in order to reduce the number of variables to a minimum (9, 10, 27).

To obtain a maximal value for interference radii we again use the example of diphenyl, assuming that the maximum intensity of absorption of a completely planar diphenyl molecule is not higher than 42,000. This value is taken as more than twice the intensity value at room temperature since instances are known where on reducing the temperature from 20° C. to about −200° C. the intensity of absorption is almost doubled (cf. 5); this change may—although this is unlikely—be ascribed entirely to increased planarity at lower temperature. Using the equation $\epsilon/\epsilon_0 = \cos^2\theta$ (8, 18) where $\epsilon_0 = 42{,}000$, for calculating the interplanar angle in 2-methyldiphenyl which absorbs maximally

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at 235 mμ (i.e. at similar wavelength compared to diphenyl) with $\epsilon = 10{,}500$ (7), we obtain a maximum interplanar angle of 60°. This leads to an interatomic distance of 2.86 Å between the hydrogen atom and the methyl-group, which corresponds to maximal values for hydrogen of 0.99 Å and 1.87 Å for the methyl-group (it is assumed that the maximum values are proportional to the minimum values).

The maximum value of 60° for the interplanar angle also appears reasonable, since it has been assumed (22) that at an angle of 67.5° there will be no conjugation between the two planar entities of the diphenyl molecule. 2-Methyldiphenyl, however, still exhibits some conjugation as compared to, for example, 2,2′-dimethyldiphenyl which only has an inflection at 227 mμ, $\epsilon = 6800$, indicating almost complete loss of cross-conjugation.

Using a similar argument for benzaldehydes—namely assuming an intensity of absorption for a planar benzaldehyde molecule of $\epsilon = 28{,}000$—we can calculate the maximum interplanar angle of 2,6-dimethylbenzaldehyde (which absorbs with $\epsilon = 12{,}500$ at comparable wavelength to benzaldehyde) to be 48°. This leads to a maximum interference value of 1.15 Å for oxygen (in C=O), using the previously obtained value of 1.7 Å for the methyl-group.

The final values therefore suggested for the effective interference radii are as follows:

H, 0.95±0.1 Å;
O (in C=O), 1.0±0.15 Å;
CH_3, 1.7±0.2 Å.

EXPERIMENTAL PART

Redistilled toluene had a boiling point of 111°, n_D^{20} 1.4960; *p*-xylene had a melting point of 13°. After fractionation under nitrogen, acrolein distilled at 52°, 769 mm., n_D^{20} 1.3998, and methylvinyl ketone at 34°, 130 mm., n_D^{20} 1.4086; 4-methyldiphenyl had a melting point of 45°. Methylvinyl ketone was prepared by the method of Wohl and Prill (29) and 4-methyldiphenyl by the method of Elks, Hayworth, and Hey (15).

The light absorption properties of the above-described compounds are recorded in Table III. The spectra were determined in duplicate by standard methods with 1 cm. cells using a Unicam SP500 spectrophotometer. Spectra, unless otherwise stated, are recorded in ethanolic solution. The determinations involving acrolein and methylvinyl ketone were carried out by direct addition of the substances to a known amount of solvent; the mixture was then diluted to the required concentration and the absorption intensity at maximal wavelength determined as quickly as possible.

ACKNOWLEDGMENTS

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They are also greatly indebted to the late Professor E. A. Braude for a number of discussions related to this general topic.

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AN EXPERIMENTAL DETERMINATION OF THE SURFACE ENTHALPY OF SODIUM CHLORIDE[1]

By G. C. Benson, H. P. Schreiber,[2] and F. van Zeggeren[3]

ABSTRACT

The surface enthalpy of NaCl has been redetermined from heats of solution of salt samples of different specific surface areas. Special care was taken in the preparation of these samples to avoid contamination by nitrate and excess sodium. The value obtained, 276 ergs/cm.^{2}, differs from that reported by Benson and Benson, viz. 305 ergs/cm.^{2}, for samples containing some nitrate impurity.

INTRODUCTION

Recently Benson and Benson (1) determined the surface enthalpy of sodium chloride by measuring heats of solution for samples of varying specific surface area. The differences of these heats of solution from that of bulk sodium chloride, when plotted as a function of the surface area, gave a straight line indicating that the deviation could be considered as a surface property to a good approximation. The slope of the least square line through the points obtained led to a value of 305 ergs/cm.^{2} for the surface enthalpy at 298° K. and this was attributed to the {100} face of the crystal. However, the line also had a negative intercept of -5.4 cal./mole which appeared to be due to some impurity in the fine salt. Prior to this, the only indications of contamination noted were the occurrence of a slight blue color in some samples and an alkaline pH for solutions of these samples in water, both suggesting the presence of excess sodium in the lattice. Since material of this kind was not used for the calorimetric measurements the negative intercept could not have been due to non-stoichiometric sodium. Furthermore, in view of the sign of the intercept, the impurity most probably had a negative heat of solution in water. It was found that material used in the calorimetric work gave a positive spot test for nitrite or nitrate. Further investigations (11) have confirmed the presence of sodium nitrate in material prepared under similar conditions.

The heat of solution of sodium nitrate in water is negative and since its magnitude is roughly four times that of sodium chloride, the percentage of sodium nitrate present in the fine salt used by Benson and Benson appears to have been relatively small (about 0.3%). Since the various specific surface areas were obtained by sintering the same starting material, a small amount of nitrate would probably have little effect on the slope of the line provided it was uniformly distributed through the bulk of the particles. On the other hand if there was a tendency for the impurity to concentrate in the surface, some influence on the surface enthalpy is quite conceivable, and the value reported by Benson and Benson was stated to be provisional. In the present paper a redetermination of the surface enthalpy of sodium chloride is described.

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[2]*National Research Laboratories Postdoctorate Fellow 1953–55. Present address: Central Research Laboratories, Canadian Industries Limited, McMasterville, Quebec.*
[3]*National Research Laboratories Postdoctorate Fellow 1955–.*

EXPERIMENTAL

The fine salt was prepared as in previous work by the electrostatic precipitation of a sodium chloride smoke. The occurrence of nitrate and excess sodium in the product has been studied by van Zeggeren, Schreiber, and Benson (11). Two factors which play an important role in the formation of these impurities are the oxygen content of the carrier gas and the precipitator voltage. In the present work a nitrogen carrier gas containing 0.05% oxygen and a precipitator voltage of 8 kv. were used. As stated in Reference 11 these conditions lead to a nitrate content of less than 0.05%. Checks were also made on the alkalinity of the salt.

Most of the samples with different surface areas were obtained from 12 independent preparations but a few of the low area samples were made by the thermal sintering of higher area material. Determinations of the surface areas were carried out according to the B.E.T. method and the values are based on a nitrogen molecular area of 16.2 Å^2. Most of the isotherms obtained for nitrogen on sodium chloride gave slightly curved B.E.T. plots in the usual p/p_0 range (0.05 to 0.3) and led to small negative intercepts when fitted with a line in this region. Points in the p/p_0 range 0.01 to 0.1 gave linear B.E.T. plots with small positive intercepts and this pressure region was used for the area

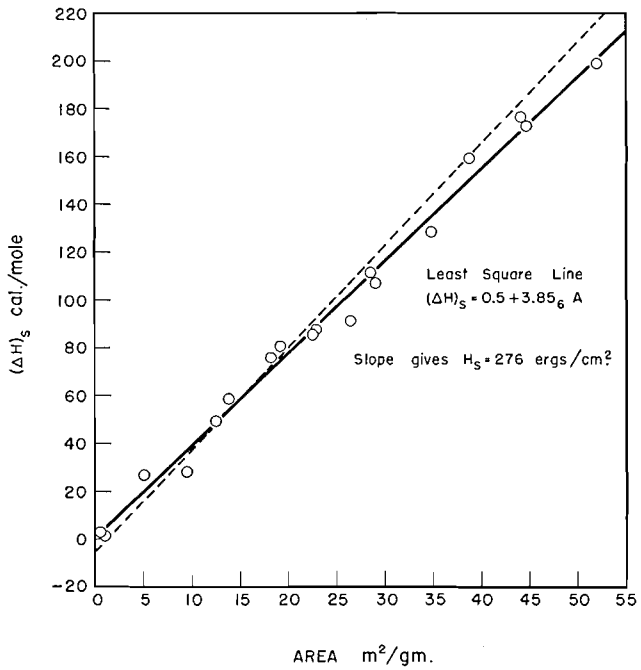

FIG. 1. Plot of the variation of the ΔH for solution of sodium chloride in water at 25° C. as a function of the surface area of the sample. The solid line drawn through the new data corresponds with a surface enthalpy of 276 ergs/cm.^{2} For comparison the results obtained in Reference 1 are indicated by the dashed line, the slope of which corresponds with a surface enthalpy of 305 ergs/cm.^{2}

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determinations in the present work rather than the range 0.05 to 0.3 employed previously.* The effect of this change on the area is relatively small.

The calorimetric techniques used were the same as described in References 1 and 2. The deviation, $(\Delta H)_s$, of the enthalpy of solution of fine salt from that of bulk material has been plotted as a function of the specific surface area in Fig. 1.

DISCUSSION

The least square line through the points of Fig. 1 has an intercept of +0.5 cal./mole. The probable error of this intercept, calculated from the formulae of Birge (4), is 1.8 cal./mole, which indicates that now the line can be considered to pass through the origin within the experimental error. For the contaminated salt Benson and Benson (1) reported a value −5.4 cal./mole for $(\Delta H)_s$ at zero area, with a probable error of 2.4 cal./mole. This corroborates the view that in the present experiments the sodium nitrate content of the salt was negligible. The slope of the least square line corresponds with a surface enthalpy of 276 ergs/cm.^{2}, that is about 30 ergs/cm.^{2} less than the value obtained by Benson and Benson. Since the probable error in the new result is 5 ergs/cm.^{2} and in the previous work was 6 ergs/cm.^{2}, this difference is significant and it favors the possibility suggested in the introduction that the nitrate tends to concentrate in the surface regions rather than being uniformly distributed throughout the bulk of the crystals.

The new value is still much higher than the results of theoretical calculations. Recently van Zeggeren and Benson (10) obtained a value of 187 ergs/cm.^{2} as a first approximation for the surface energy of a {100} face of sodium chloride at 0° K. from a quantum mechanical model in which no allowance was made for van der Waals forces or distortion at the surface. A theoretical estimate of the surface energy on the basis of a classical model is 112 ergs/cm.^{2} at 0° K. This is taken from calculations by Shuttleworth (9) with the distortion energy contribution corrected in accordance with the findings of Benson, Schreiber, and Patterson (3).

It is unlikely that the difference in temperature can account for the deviation between the experimental result for 298° K. and theoretical values calculated for 0° K. Morrison and Patterson (7) have extended the temperature range of the specific heat measurements on finely divided sodium chloride previously reported by Patterson, Morrison, and Thompson (8). Their data show a definite particle size effect but it is not simply related to the surface area of the sample and these authors suggest that the excess specific heat over that predicted by the theoretical treatment of Montroll (6) is due to a loosening of the surface structure. Until this is investigated more completely, use of the data to estimate a temperature correction of the surface enthalpy is uncertain, but a decrease of 10 to 20 ergs/cm.^{2} would appear to be an upper limit for this correction.

Recently one other experimental determination of the surface enthalpy of

*We are most indebted to Dr. P. H. Emmett and Dr. S. Brunauer for discussions and correspondence which led to the change adopted here.

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sodium chloride has been reported. Hutchinson and Manchester (5) obtained a value of 366 ergs/cm.^{2} from heats of solution of lyophilized salt. This result is rather uncertain since the surface area was estimated in an approximate manner from electron micrographs and no attempt was made to establish that the difference in the heats of solution was proportional to the specific surface area.

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SOME BASIC DERIVATIVES OF 6-CHLOROQUINAZOLINE AND PHTHALAZINE[1]

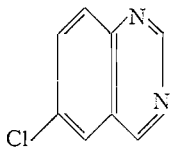
By Stanley O. Winthrop, Stella Sybulski, Roger Gaudry, and Gordon A. Grant

ABSTRACT

Basic derivatives of 6-chloroquinazoline and phthalazine have been synthesized and screened for their physiological action on the central nervous system. Sodium dialkylaminoalkoxides and the appropriate chlorobenzodiazine were brought together to yield basic ethers of 6-chloroquinazoline and phthalazine respectively. 1-(γ-Dimethylaminopropylamino)phthalazine was also prepared.

INTRODUCTION

This study represents a part of a continuing program which, it is hoped, will lead to new drugs acting on the central nervous system. It was of interest to investigate certain benzodiazine ring systems as possible carriers of groupings known to have central nervous system activity. We have investigated 6-chloroquinazoline (I) and phthalazine (II) as possible carriers of this type. The 6-chloroquinazoline was chosen rather than quinazoline itself because of its structural relationship to 3-chlorophenothiazine, a highly successful carrier.



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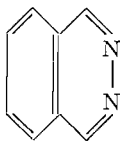

II

Sherrill (1) has described the 4-(β-diethylaminopropoxy)-6-chloroquinazoline as its phosphate salt. We were unable to prepare this phosphate but found the citrate to be a more easily obtained acid addition salt. In an analogous manner, three new 6-chloroquinazoline basic ethers were prepared and are listed in Table I.

Although 1-alkoxyphthalazines have been reported (2), no mention of a 1-dialkylaminoalkoxyphthalazine could be found in the literature. The 1-(γ-diethylaminopropoxy)phthalazine was prepared from 1-chlorophthalazine and the appropriate alcohol by the same procedure as was used for the preparation of the quinazoline ethers.

The instability of phthalazines and particularly aminophthalazines towards heat has been noted. Only a small number of 1-alkylaminophthalazines have been reported (2) and their preparation usually results in resinous by-products and consequently low yields of the aminophthalazine. 1-(γ-Dimethylamino-

[1]*Manuscript received July 11, 1956.*
Contribution from the Research Laboratories, Ayerst, McKenna & Harrison Limited, Montreal, Que.

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TABLE I

6-CHLOROQUINAZOLINES

4-Substituents	Salt	M.p., °C. (uncorr.)	Yield,[e] %	Formulae	Carbon		Hydrogen		Nitrogen		Chlorine	
					Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$(CH_3CH_2)_2NCH_2CH_2CH_2O$	Citrate	120–121[a]	41	$C_{21}H_{23}N_3O_3Cl$	51.88	51.95	5.81	5.77	8.65	8.91	7.31	7.19
$((CH_3)_2CH)_2NCH_2CH_2OCH_2CH_2O$	HCl	123–125[b]	34	$C_{18}H_{29}N_3O_2Cl_2$					10.82	10.80	18.26	18.28
$(CH_3CH_2)_2NCH_2CH_2OCH_2CH_2O$	$2H_2SO_4$	135–137[c]	24	$C_{16}H_{26}N_3O_{16}S_2Cl$	36.90	37.31	5.04	5.02	8.08	8.23	6.82	7.07
$(CH_3)_2NCH_2CH_2OCH_2CH_2O$	Maleate	111–112[b]	20	$C_{18}H_{22}N_3O_6Cl$	52.50	52.26	5.39	5.62	10.21	10.30	8.62	8.65
$(CH_3)_2NCH_2CH_2OCH_2CH_2O$		Oil[d]	52	$C_{14}H_{18}N_3O_2Cl$					14.22	14.18		

[a]*Recrystallized from isopropanol.* [b]*Recrystallized from ethylacetate.* [c]*Recrystallized from isopropanol–ether.* [d]*The base was obtained by treatment of the maleate salt with sodium carbonate solution followed by chloroform extraction. Removal of the chloroform and high vacuum drying gave a heavy oil which analyzed correctly for the free base.* [e]*The yields are based on the product as its salt after one recrystallization.*

propylamino)phthalazine was prepared from 1-chlorophthalazine and dimethylaminopropylamine. The presence or absence of a solvent did not appreciably affect the yields.

Some of the quinazolines were found to be central nervous system depressants and also showed appreciable musculotropic activity.

EXPERIMENTAL

4,6-Dichloroquinazoline

This was prepared from 5-chloroanthranilic acid by way of the 6-chloro-4-quinazolone (1). The material melted at 155–158°C. (lit. m.p. 154–155°C.).

1-Chlorophthalazine

Phthalaldehydic acid (Eastman) and hydrazine gave 1-hydroxyphthalazine which was in turn converted to 1-chlorophthalazine (2) by the action of phosphorus oxychloride. The compound melted at 114.5–115.5°C. (lit. m.p. 113°C.). 1-Chlorophthalazine had to be used fresh since it underwent a gradual transformation, on standing at room temperature, into higher melting substances.

4-(β-Dialkylaminoethoxyethoxy)-6-chloroquinazolines

The 4,6-dichloroquinazoline was allowed to react with sodium β-dialkylaminoethoxyethoxide in an excess of the aminoalcohol according to the method of Sherrill (1). The products were isolated as their acid addition salts since losses due to decomposition during an attempted vacuum distillation of one of the crude bases were excessive.

1-Dialkylaminoalkoxyphthalazines

The phthalazine basic ethers were prepared in the same manner as the quinazolines. The salts were heat sensitive and partly resinified on recrystallization. In some cases this causes losses of up to 50% and made purification difficult.

1-(γ-Dimethylaminopropylamino)phthalazine

Method A

1-Chlorophthalazine, 7.5 gm., 0.045 mole, and 9.2 gm., 0.09 mole, dimethylaminopropylamine were dissolved in 75 ml. of absolute alcohol and warmed on a water bath at 70°C. for seven hours. On cooling and addition of ether, dimethylaminopropylamine hydrochloride precipitated and was filtered off. The filtrate was evaporated down *in vacuo* at room temperature, leaving 10 gm. of a heavy oily residue. Ethereal hydrogen chloride was carefully added to an ether solution of the oil residue and the product precipitated as the dihydrochloride, 3.7 gm., m.p. 246–248°C. Two recrystallizations from ethanol–ether gave 1.4 gm. of a hygroscopic dihydrochloride, m.p. 242–243°C. (see Table II).

Method B

1-Chlorophthalazine, 7.5 gm., 0.045 mole, and 18.4 gm., 0.18 mole, dimethylaminopropylamine were warmed together on a water bath at 70°C. for

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TABLE II

PHTHALAZINES

1-Substituents	Salt	M.p., °C.[a] (uncorr.)	Yield,[b] %	Formulae	Carbon		Hydrogen		Nitrogen		Halogen	
					Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$(CH_3CH_2)_2NCH_2CH_2CH_2O$	Citrate $.H_2O$	129.5–130.5[d]	10	$C_{21}H_{31}N_3O_9$	53.65	53.95	6.65	6.61	8.94	9.07		
$(CH_3CH_2)_2NCH_2CH_2CH_2O$	$2CH_3I$	168.5–169.5[e]	21	$C_{17}H_{27}N_3OI_2$					7.75	7.93	46.73	46.13
$((CH_3)_2CH)_2NCH_2CH_2OCH_2CH_2O$	2HCl	118–120[f]	16	$C_{18}H_{29}N_3O_2Cl_2$					10.78	10.99		
$((CH_3)_2CH)_2NCH_2CH_2OCH_2CH_2O$	$2CH_3I$	163–165[c]	17	$C_{20}H_{33}N_3O_2I$					6.99	7.14	42.24	42.00
$(CH_3)_2NCH_2CH_2CH_2NH$	2HCl	242–243[c]	27	$C_{13}H_{20}N_4Cl_2$[c]	51.43	51.05	6.65	7.07			23.42	22.95
$(CH_3)_2NCH_2CH_2CH_2NH$	$2CH_3I$	235–237[c]	27	$C_{16}H_{26}N_4I_2$					10.58	10.56	48.05	48.17

[a]*Melting points were determined by placing the compound in the bath 15 degrees below the approximate melting point and increasing the temperature 2 degrees a minute. Variations in melting points occurred depending on the method used since the phthalazines are heat sensitive.* [b]*The yields are based on the product as its salt after one recrystallization. The yields before purifications were considerably greater than these recorded here.* [c]*This compound was very hygroscopic. Karl Fischer's analysis gave 6.02% water. The analyses are based on the dry weight.* [d]*Recrystallized from methanol–ether.* [e]*Recrystallized from ethanol–ether.* [f]*Recrystallized from isopropanol–ether.*

seven hours. The reaction mixture was then taken up in isopropanol–ether and the dimethylaminopropylamine hydrochloride precipitated. The filtrate was worked up as in Method A and the excess amine removed by vacuum distillation at 3 mm. The pot residue, a reddish oil, 11.1 gm., was taken up in acetone and treated with methyl iodide to yield 10.4 gm. of a bismethiodide salt, m.p. 236–238°C. Two recrystallizations from ethanol–ether gave 5.8 gm. of an analytically pure compound, m.p. 235–237°C.

ACKNOWLEDGMENTS

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AN IMPROVED SYNTHESIS OF ACETOSYRINGONE[1]

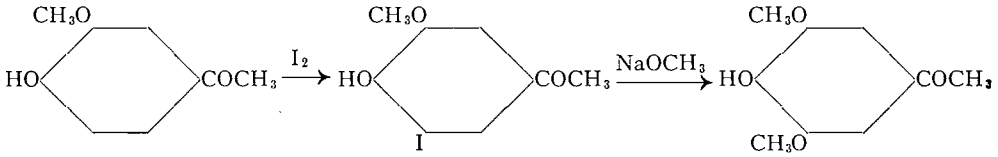
By L. W. Crawford, E. O. Eaton, and J. M. Pepper

ABSTRACT

Acetosyringone has been synthesized from acetovanillone, in better than a 50% yield, through conversion to 5-iodoacetovanillone followed by its interaction with sodium methoxide in the presence of copper catalyst. The previously unreported intermediate, 5-iodoacetovanillone, was characterized by methylation to 5-iodoacetoveratrone and subsequent oxidation to the known 5-iodoveratric acid.

One of the more fruitful fields of research on the chemical structure of lignin has been that of oxidation (3). By means of the alkaline nitrobenzene oxidation of wood meal itself, or of isolated lignins, good yields of the phenolic aldehydes vanillin and syringaldehyde have been obtained, along with lesser amounts of acetovanillone* (4-hydroxy-3-methoxyphenyl methyl ketone) (I) and acetosyringone* (4-hydroxy-3,5-dimethoxyphenyl methyl ketone) (III). With respect to the structure of lignin the latter two derivatives, being C_6—C—C fragments, are of more structural significance than the former more highly degraded C_6—C derivatives. In order to study the problems associated with the separation of these four lignin derivatives from admixture, it was necessary to have available pure samples of each compound. Vanillin and acetovanillone are available commercially and syringaldehyde may be synthesized by any of several methods (1, 11, 10, 13), but the reported syntheses of acetosyringone have been difficult and have resulted in poor over-all yields. The present work describes an improved two-stage synthesis of acetosyringone from acetovanillone.

Synthetic acetosyringone was reported first by Bradley and Robinson (2), who used a multistep synthesis starting from O-benzylsyringoyl chloride and ethyl acetoacetate, and who reported that their product melted at 117°C. Later, Mauthner (8) described the more direct synthesis involving the aluminum chloride catalyzed rearrangement of 2,6-dimethoxyphenyl acetate. Leger and Hibbert (7) and later Pepper and Hibbert (12) used this method of Mauthner and prepared acetosyringone melting at 120.5–121.5°C. and 121–122°C. and in yields of 11 and 12.6% respectively. A new synthesis has been effected starting from acetovanillone (I) according to the following equations:



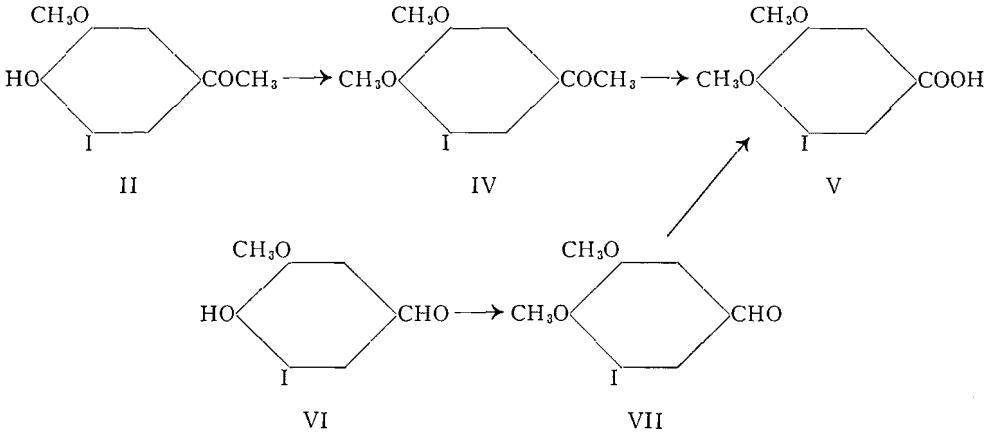
I II III

[1]*Manuscript received June 25, 1956.*
Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask.
**The names acetovanillone and acetosyringone and those of their corresponding derivatives are used extensively in the literature and hence are used throughout this paper.*

The procedure of Carles (4) for the iodination of vanillin, involving the addition of a methanolic solution of iodine to a warmed aqueous solution of vanillin, was applied to the iodination of acetovanillone, and a product obtained in 5.6% yield, after recrystallization from acetic acid, m.p. 175–177°C. A modification of the procedure used by Erdtman (5) for the synthesis of 5-iodovanillin, whereby the sodium hydroxide was replaced by sodium carbonate, gave rise to an iodinated derivative, in 82.5% yield, m.p. 172–174°C. No depression of melting points was found in admixture of samples of the iodinated products made by the two methods.

Since 5-iodoacetovanillone was previously unreported, it was first necessary to prove the structure of the iodinated product. The position of the ring-substituted iodine could be proved if the unknown were oxidized to a product identical with an authentic sample of 5-iodovanillic acid. All attempts to isolate 5-iodovanillic acid from the alkaline liquors of either sodium hypoiodite or sodium hypobromite oxidations were unsuccessful. Fuson and Bull (6) have reported that haloform reactions on either hydroxy- or nitro-acetophenones do not result in formation of the expected acids even though the haloform itself may be formed. Attempts to oxidize 5-iodovanillin by the method of Pearl (9), using silver oxide, were also unsuccessful.

The following series of reactions served to characterize the unknown as 5-iodoacetovanillone.



The unknown was converted by methylation to 5-iodoveratryl methyl ketone (IV) and hence to 5-iodoveratric acid (V) by oxidation with potassium permanganate. This last compound was identical with a sample of the acid prepared by the methylation of 5-iodovanillin (VI) to 5-iodoveratraldehyde (VII) followed by oxidation.

The 5-iodoacetovanillone was then converted to acetosyringone (III) by a procedure similar to that whereby 5-iodovanillin had been converted to syringaldehyde (13), i.e. by the interaction with methanolic sodium methoxide at elevated temperatures in the presence of copper catalyst. The crude acetosyringone was purified by recrystallization from water. The results of six such experiments are given in Table I.

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TABLE I

REACTION OF 5-IODOACETOVANILLONE WITH SODIUM METHOXIDE USING COPPER CATALYST

Run	Temp., °C.	Time, hr.	MeOH-sol.,* gm.	Acetosyringone			
				From water		From mother liquor	
				Wt., gm.	M.p., °C.	Wt., gm.	M.p., °C.
1	149–151	1	8.0	4.1	116–123	1.5	60–90
2	141–144	1	8.8	4.9	113–120	1.8	65–110
3	133–135	1	10.0	4.1	110–121	—	—
4	135	†	6.0	1.5	115–120	2.2	98–105
5	136–139	0.5	8.2	2.7	115–121	3.2	98–110
6	135–137	4.75	10.0	4.0	119–122	1.0	119–123

**Theoretical yield of acetosyringone, 9.4 gm.*
†Reaction mixture heated to 135°C., then cooled immediately.

EXPERIMENTAL

All melting points were determined using a Fisher-Johns melting point apparatus and are uncorrected.

Synthesis of 5-Iodoacetovanillone

(*a*) Acetovanillone (5.1 gm.) was dissolved in water (100 ml.) and a solution of iodine (3.0 gm.) in methanol (100 gm.) was added. The mixture was well stirred and maintained at a temperature of 50°C. for 24 hr. After the mixture was cooled, the resultant precipitate was removed by filtration and was recrystallized from acetic acid, to yield a product (0.5 gm., 5.6%), m.p. 175–177°C.

(*b*) Acetovanillone (50 gm.) and sodium bicarbonate (16.0 gm.) were dissolved, with warming, in water (300 ml.). To this a solution of iodine (75.6 gm.) dissolved in a solution of potassium iodide (85.0 gm.) in water (400 ml.) was added slowly with stirring whilst the temperature was maintained at 80°C. After the addition of approximately 25% of the iodine solution a yellow precipitate appeared. After complete addition, the resultant solution was decolorized with a minimum quantity of sodium thiosulphate and filtered while hot. After the precipitate collected, it was washed with water (500 ml.) and dried; yield 72.5 gm., 82.5%, m.p. 172–174°C. After recrystallization of the precipitate from ethanol–water, then ethanol, the melting point was 178–179°C. Calc. for $C_9H_9O_3I$: C, 37.00; H, 3.11%. Found: C, 37.02; H, 3.11%. The *p*-nitrophenylhydrazone melted at 212–213°C. A mixed melting point with the sample prepared by Carles' method gave no depression.

Characterization of 5-Iodoacetovanillone. 5-Iodoveratraldehyde

5-Iodovanillin (3 gm.) and sodium bicarbonate (20 gm.) were heated in water (100 ml.) to 55°C. Dimethyl sulphate (6.7 gm.) was added dropwise during one half hour, the temperature being maintained at 55°C. On cooling, the mixture was extracted with ether (100 ml.), and the ether extract washed with *N* sodium hydroxide, dried, and concentrated to yield white crystals; yeild 1.24 gm., m.p. 70–72°C.; reported m.p. 72–73°C. (14).

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5-Iodoveratric acid from 5-iodoveratraldehyde.—5-Iodoveratraldehyde (1.24 gm.) was added to pyridine (6 ml.) and the mixture maintained at 55°C. during the slow addition of potassium permanganate (5%, 8 ml.). After removal of the precipitated manganese dioxide, the filtrate was discolored with a little sodium bisulphite, poured into water, and acidified with concentrated hydrochloric acid. The crude product that precipitated (0.67 gm., 51%), m.p. 179–180°C., was purified by reprecipitation, by acidification, from an ether-extracted alkaline solution; m.p. 183–183.5°C.; reported m.p. 184–185°C. (13).

5-Iodoacetoveratrone.—A solution of 5-iodoacetovanillone (1.2 gm.), dimethyl sulphate (2.7 gm.), and ethanol (7 ml.) was heated to reflux. Sodium hydroxide (10 *N*, 3 ml.) was added dropwise over a period of 15 min. After the further addition of dimethyl sulphate (2.7 gm.), sodium hydroxide (10 *N*, 3 ml.), the mixture was refluxed for one-half hour and poured into water (200 ml.). The alkaline solution was extracted with ether (2 × 50 ml.); the extract, after drying and concentration, yielded crude 5-iodoacetoveratrone, 1.0 gm. (79%), m.p. 73–77°C. Recrystallization from ethanol–water, then ethanol, gave white crystals, m.p. 78–79°C. Calc. for $C_{10}H_{11}O_3I$: C, 39.23; H, 3.62%. Found: C, 39.17; H, 3.64%. No previous report on this compound could be found.

5-Iodoveratric acid from 5-iodoacetoveratrone.—5-Iodoacetoveratrone (1.0 gm.) was dissolved in pyridine (10 ml.) and the mixture heated to 60°C. during the addition of potassium permanganate (5%, 30 ml.) in 5 ml. portions. After removal of the manganese dioxide, the filtrate was discolored with sodium bisulphite, made alkaline with sodium hydroxide, and extracted with ether. The aqueous layer, after acidification, was extracted with ether (100 ml.). From this extract, after drying and concentration, 5-iodoveratric acid was obtained (0.33 gm., 33%), m.p. 183–184°C. A mixed melting point determination on samples of the acid made by both methods showed no depression.

Acetosyringone

A typical synthesis is as follows: Sodium (12 gm.) was dissolved in anhydrous methanol (300 ml.) and this solution together with copper powder (B.D.H. precipitated, 7.7 gm.) and 5-iodoacetovanillone (14 gm.) was heated, with shaking, in a bomb, capacity 1410 ml., of an Aminco high pressure hydrogenator, Model No. 406-01DA. Temperature control was ±4°C. At the end of the specified reaction time the bomb was cooled and the contents rinsed into a beaker with water (600 ml.) The copper catalyst was removed by filtration and the filtrate acidified with concentrated hydrochloric acid. This precipitated any unchanged 5-iodoacetovanillone, which was much less soluble, *ca.* 1/200, than the required acetosyringone. The filtrate was extracted with chloroform (6 × 200 ml.) and the extract was then washed with 5% sodium thiosulphate (100 ml.), then with water (2 × 100 ml.), and finally evaporated under reduced pressure to dryness. The residue was extracted with methanol (100 ml.) whereby some red colored impurities were separated as a methanol-insoluble portion. Evaporation of the methanol gave the crude acetosyringone, which was crystallized from water. A sample recrystallized

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from water, then Skellysolve "C", melted at 123–124°C.; reported m.p. 121–122°C. (12). Calc. for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17%. Found: C, 61.40; H, 6.14%. The *p*-nitrophenylhydrazone melted at 193.5–194.5°C.; reported m.p. 194.5–195.5°C. (7).

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1-(β-DIALKYLAMINOETHYL)-2-IMIDAZOLIDINETHIONES[1]

By A. F. McKay, D. L. Garmaise, and A. Halasz

ABSTRACT

A series of 1-(β-dialkylaminoethyl)-2-imidazolidinethiones and their picrates are described. 1-(β-Diethylaminoethyl)-2-methylmercapto-2-imidazoline dihydroiodide combined with benzylamine with the evolution of methyl mercaptan to give 1-(β-diethylaminoethyl)-2-benzylamino-2-imidazoline (III). In a similar reaction β-alanine gave a product whose picrate gave analytical values in agreement with those calculated for the dipicrate of 1-(β-diethylaminoethyl)-5-keto-Δ^8-hexahydro-1,4,8-pyrimidazole (IV).

Recently the preparation and properties of a series of 1-alkyl-2-imidazolidinethiones were described by Thorn (11). A similar method of preparation has been used to prepare 1-(β-hydroxyethyl)-2-imidazolidinethione (8), 1-isopropylhexahydropyrimidine-2-thione (7), and a series of 1-(β-dialkylaminoethyl)-2-imidazolidinethiones. The 1-(β-dialkylaminoethyl)-2-imidazolidinethiones and their picrates are described in Table I. During the course of this work 1-isopropoxypropyl-2-imidazolidinethione also was prepared.

The amines required for the syntheses of the 1-(β-dialkylaminoethyl)-2-imidazolidinethiones were prepared by the addition of ethylenimine to the corresponding dialkylamines (4, 5). The properties of these amines and their picrates are given in Tables II and III respectively.

1-(β-Diethylaminoethyl)-2-imidazolidinethione was converted to its hydroiodide salt (I) and then methylated with methyl iodide. This procedure eliminated the possibility of methylating the diethylamino group and 1-(β-diethylaminoethyl)-2-methylmercapto-2-imidazoline dihydroiodide (II) was obtained in good yield (92.5%). Compound II on refluxing with 1 mole equivalent of benzylamine in the presence of methanol evolved methyl mercaptan. The product on treatment with aqueous picric acid gave a dipicrate melting at 210–211°C. This picrate on analysis gave values in good agreement with the dipicrate salt of structure III ($R = C_6H_5CH_2$). This reaction is analogous to previously described reactions of amines with 2-methylmercapto-2-imidazolines (2, 7, 8) and 2-methylmercapto-2-oxazolines (10).

Several attempts to prepare 1-(β-diethylaminoethyl-2-(β-carboxyethyl)-2-imidazoline by the reaction (6, 7) used in the synthesis of cyclic guanidino acids gave variable results. In some runs large amounts of unreacted β-alanine were recovered. Three runs produced a viscous oil which on treatment with aqueous picric acid gave a picrate melting at 176.5–177°C. This compound gave analytical values in excellent agreement with the calculated for the dipicrate of structure IV. Compounds similar to structure IV have been prepared (7) from cyclic guanidino acids.

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Contribution from the L. G. Ryan Research Laboratories of Monsanto Canada Limited, Ville LaSalle, Quebec.

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TABLE I

1-(β-DIALKYLAMINOETHYL)-IMIDAZOLIDINE-2-THIONES AND THEIR PICRATES

Alkyl group	Yield, %	M.p., °C.	Formula	C		H		N		S	
				Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
CH_3	54.0	94–95	$C_7H_{15}N_3S$	48.53	48.61	8.73	8.63	24.25	24.50	18.50	18.65
		166–167[a]	$C_{13}H_{18}N_6SO_7$	38.81	38.82	4.51	4.51	20.88	20.60	7.97	7.86
C_2H_5	75.7	77–78	$C_9H_{19}N_3S$	53.70	53.97	9.51	9.71	20.88	20.50	15.93	16.10
		141–142[a]	$C_{15}H_{22}N_6SO_7$	41.86	41.94	5.15	5.33	19.53	19.80	7.45	7.75
n-C_3H_7	31.4	74–75	$C_{11}H_{23}N_3S$	57.58	57.31	10.10	9.99	18.32	18.20	13.97	14.15
		124–125[a]	$C_{17}H_{26}N_6SO_7$	44.49	44.59	5.72	5.70	18.33	17.97	6.99	6.83
n-C_4H_9	57.0	43–44	$C_{13}H_{27}N_3S$	60.64	60.64	10.58	10.83	16.33	16.20	12.45	12.40
		115–117[a]	$C_{19}H_{30}N_6SO_7$	46.89	46.81	6.21	6.28	17.28	16.98		

[a]*Picrates.*

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TABLE II

POLYAMINES

Compound	Yield,[a] %	Boiling point		n_D	
		°C.	mm. pressure	°C.	Reading
$(CH_3)_2N(CH_2)_2NH_2$[b]	54.5–60.0	104–106	760	25	1.4250
$(CH_3)_2N(CH_2)_2NH(CH_2)_2NH_2$	9.2–17.7	169–180	760	25	1.4583
$(C_2H_5)_2N(CH_2)_2NH_2$[c]	37.5–41.0	78–80	60	25	1.4362
		146–150	760		
$(C_2H_5)_2N(CH_2)_2NH(CH_2)_2NH_2$[d]	17.0–23.2	108–110	19	25	1.4539
		114–116	25		
$(n\text{-}C_3H_7)_2NH(CH_2)_2NH_2$[e]	28.6	96–98	41	23	1.4384
$(n\text{-}C_3H_7)_2NH(CH_2)_2NH(CH_2)_2NH_2$	23.3	154–160	41	23	1.4570
$(n\text{-}C_4H_9)_2NH(CH_2)_2NH_2$[f]	29.4–31.6	114–117	24	26	1.4410
$(n\text{-}C_4H_9)_2NH(CH_2)_2NH(CH_2)_2NH_2$	16.2–17.0	155–164	24	23.5	1.4589
$i\text{-}C_3H_7O(CH_2)_3NH(CH_2)_2NH_2$	8.9	120–124	24	22	1.4465

[a] *The yields reported within ranges represent several runs.*

[b] *Turner (12) reports b.p. 105–108°C.*

[c] *Bloom et al. (3) report b.p. 144–145° at 760 mm.*

[d] *Braz and Skorodumov (4) report b.p. 112–114° at 24 mm., and* n_D^{20} *1.4629.*

[e] *Braz and Skorodumov (4) report b.p. 87–88° at 29 mm., and* n_D^{20} *1.4487.*

[f] *Braz and Skorodumov (4) report b.p. 107° at 21 mm., and* n_D^{20} *1.4449. Amundsen and Krantz (1) report b.p. 98–101° at 13 mm.*

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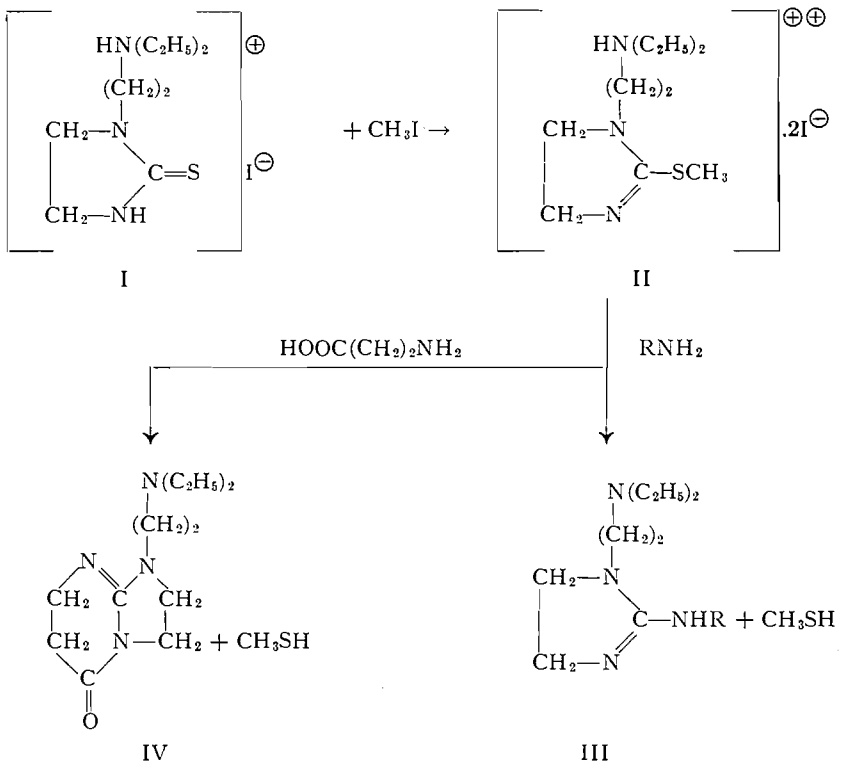
TABLE III

PICRATES OF POLYAMINES

Compound	M.p., °C. (dec.)	Formula	C		H		N	
			Calc.	Found	Calc.	Found	Calc.	Found
$(CH_3)_2NH(CH_2)_2NH_2$	228–229	$C_{16}H_{19}N_8O_{14}$	35.10	35.36	3.49	3.42	20.51	20.20
$(CH_3)_2NH(CH_2)_2NH(CH_2)_2NH_2$	209–209.5	$C_{24}H_{27}N_{12}O_{21}$	35.18	35.23	3.32	3.41	20.50	20.10
$(C_2H_5)_2NH(CH_2)_2NH_2$[a]	214–215							
$(C_2H_5)_2NH(CH_2)_2NH(CH_2)_2NH_2$[b]	206–207							
$(n\text{-}C_3H_7)_2NH(CH_2)_2NH_2$[c]	192–192.5							
$(n\text{-}C_3H_7)_2NH(CH_2)_2NH(CH_2)_2NH_2$	204–205	$C_{28}H_{35}N_{12}O_{21}$	38.41	38.86	4.03	4.07	19.20	19.50
$(n\text{-}C_4H_9)_2NH(CH_2)_2NH_2$[d]	192–193							
$(n\text{-}C_4H_9)_2NH(CH_2)_2NH(CH_2)_2NH_2$	209–210	$C_{30}H_{39}N_{12}O_{21}$	39.88	40.03	4.35	4.18	18.60	18.59
$i\text{-}C_3H_7O(CH_2)_3NH(CH_2)_2NH_2$	146	$C_{20}H_{26}N_8O_{15}$	38.89	38.93	4.08	4.27	18.13	17.90

[a] *Ristenpart (9) reports m.p. 211°C.*
[b] *Braz and Skorodumov (4) report m.p. 204.5–205.5°C.*
[c] *Braz and Skorodumov (4) report m.p. 192–193.5°C.*
[d] *Braz and Skorodumov (4) report m.p. 187–189°C.*



EXPERIMENTAL[2]

The Addition of Amines to Ethylenimine

The amines described in Table I were prepared by the addition of ethylenimine to the corresponding monoamino derivative by the method of Braz and Skorodumov (4, 5). Their picrates listed in Table II were obtained from their aqueous solutions on addition of saturated aqueous picric acid solution.

In one experiment the primary addition product, N,N-diethyl ethylenediamine (116 gm., 1.0 mole), was refluxed in an absolute ethanol (250 cc.) solution of ethylenimine (21.5 gm., 0.50 mole) in the presence of N,N-diethyl ethylenediamine dihydrochloride (1.4 gm., 0.0075 mole) for 11 hr. After the ethanol was removed by evaporation, the residue was fractionally distilled. In addition to the expected secondary product, N,N-diethyl-N′-(2-aminoethyl) ethylenediamine (b.p. 114–116°C. at 25 mm.; n_D^{25} 1.4539; yield 37.1 gm.; 46.7%), part of the N,N-diethyl ethylenediamine was recovered unchanged. A residue (22 gm.) of higher order addition products also was obtained.

1-(β-Dialkylaminoethyl)-2-imidazolidinethiones

The 1-(β-dialkylaminoethyl)-2-imidazolidinethiones described in Table I were prepared in a similar manner and only the preparation of one of them is given below in detail.

[2]*All melting points are uncorrected. The microanalyses were determined by Micro Tech Laboratories, Skokie, Illinois.*

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N,N-Diethyl-N′-(2-aminoethyl) ethylenediamine (109 gm., 0.686 mole) in benzene (250 cc.) was treated with carbon disulphide (58 gm., 0.75 mole) in benzene (100 cc.) under the conditions previously described (7) for the preparation of hexahydropyrimidine-2-thione. The benzene was removed *in vacuo* and the residue was heated at 150°C. for 30 min. under nitrogen at 30 mm. pressure. The residue was extracted with boiling petroleum ether (65–105°C.) (5 × 1 liter). The insoluble residue (16.2 gm.) was discarded. After the petroleum extract was concentrated to 3 liters, crystals (m.p. 74–77°C.) of 1-(β-diethylaminoethyl)-2-imidazolidinethione separated, yield 105 gm. (75.7%). One crystallization from ether (4 cc. per gm.) raised the melting point to a constant value of 77–78°C.

A small sample of the final product was converted into its picrate in aqueous solution in the usual manner. The properties of the picrates of the 1-(β-dialkylaminoethyl)-2-imidazolidinethiones are given in Table I.

1-(γ-Isopropoxypropyl)-2-imidazolidinethione

Crude 1-(γ-isopropoxypropyl)-2-imidazolidinethione was prepared in 70% yield by the method described above for the preparation of the 1-substituted-2-imidazolidinethiones. The product was purified by several crystallizations from ether after which it melted at 56–57°C. The yield of pure product was 36%. Anal. Calc. for $C_9H_{18}N_2OS$: C, 53.44; H, 8.97; N, 13.85; S, 15.85%. Found: C, 53.62; H, 8.84; N, 13.56; S, 16.03%.

1-(β-Diethylaminoethyl)-2-methylmercapto-2-imidazoline Dihydroiodide

Aqueous hydrogen iodide solution (55%) was added dropwise to a solution of 1-(β-diethylaminoethyl)-2-imidazolidinethione (40.26 gm., 0.2 mole) in methanol (100 cc.) at 10–12°C. until a pH of 5.0 was attained. The solution on being cooled to 0°C. gave 40.1 gm. of the hydroiodide salt (m.p. 116–118°C.). Another crop of 20.8 gm. of the hydroiodide salt (m.p. 116–118°C.) was obtained by dilution of the filtrate with ether (100 cc.). The total yield was 92.5%. The melting point was raised to a constant value of 117–118°C. by two crystallizations from absolute ethanol. Anal. Calc. for $C_9H_{20}IN_3S$: C, 32.98; H, 5.93; N, 12.50%. Found: C, 32.82; H, 6.12; N, 12.76%.

A solution of the hydroiodide salt of 1-(β-diethylaminoethyl)-2-imidazolidinethione (58.9 gm., 0.179 mole) and methyl iodide (26.2 gm., 0.185 mole) in methanol (100 cc.) was refluxed for 15 min. After removal of the methanol by evaporation, a crystalline residue (m.p. 120–126°C.) of 1-(β-diethylaminoethyl)-2-methylmercapto-2-imidazoline dihydroiodide was obtained, yield 84.4 gm. (99.8%). Several crystallizations from ethanol raised the melting point to 127–129°C. Anal. Calc. for $C_{10}H_{23}I_2N_3S$: C, 25.49; H, 4.92; N, 8.92%. Found: C, 25.80; H, 5.15; N, 8.62%.

1-(β-Diethylaminoethyl)-2-benzylamino-2-imidazoline Dipicrate

A solution of 1-(β-diethylaminoethyl)-2-methylmercapto-2-imidazoline dihydroiodide (47.1 gm., 0.10 mole) and benzylamine (10.7 gm., 0.10 mole) in methanol (30 cc.) was refluxed for 30 min. After removal of the methanol by evaporation, a semisolid was obtained, yield 42 gm. A portion (2.8 gm.) of

this material was dissolved in water (15 cc.) and saturated aqueous picric acid solution was added. The crude dipicrate (m.p. 170–180°C.) was obtained in 34.8% yield based on the dihydroiodide salt. One crystallization from water raised the melting point to a constant value of 210–211°C. Anal. Calc. for $C_{28}H_{32}N_{10}O_{14}$: C, 45.89; H, 4.41; N, 19.12%. Found: C, 46.09; H, 4.65; N, 18.90%.

Condensation of β-Alanine with 1-(β-Diethylaminoethyl)-2-methylmercapto-2-imidazoline

1-(β-Diethylaminoethyl)-2-methylmercapto-2-imidazoline dihydroiodide (9.4 gm., 0.02 mole) was added to a solution of sodium hydroxide (2.0 gm., 0.05 mole) in water (10 cc.) at 0°C. The solution was extracted with chloroform (3 × 50 cc.) and the chloroform solution was dried over anhydrous sodium sulphate and evaporated. The residue weighed 4.4 gm. (theory 4.3 gm.) and the free base must have been contaminated with some salt.

A portion of the free base (0.80 gm., 0.0037 mole) and β-alanine (0.27 gm., 0.003 mole) were dissolved in absolute methanol (15 cc.) and the solution was refluxed for three hours. During this time methyl mercaptan was evolved. After the methanol was removed by evaporation a gummy product was obtained. The product on treatment with aqueous picric acid solution gave 0.26 gm. (17.34%) of picrate melting at 170–174°C. One crystallization from methanol raised the melting point to 176.5–177°C. Anal. Calc. for $C_{24}H_{28}N_{10}O_{15}$: C, 41.36; H, 4.19; N, 20.08%. Found: C, 41.49; H, 4.18; N, 20.18%.

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RADIOCHEMICAL STUDIES OF GRAPHITE FERRIC CHLORIDE[1]

By R. M. Lazo[2] and J. G. Hooley

ABSTRACT

Graphite ferric chloride, $C_{12}FeCl_3$, was prepared by heating anhydrous ferric chloride with graphite at 305°C. The purified compound containing 53% ferric chloride was not attacked by hot 6 *N* hydrochloric acid and gave an X-ray diffraction pattern which was distinctly different from that of either graphite or ferric chloride. The separation of the graphite layer-planes was increased from 3.36 to 9.4 Å by the intercalation of the ferric chloride molecules.

Tests for exchange between $C_{12}FeCl_3$ and Fe^{+++} ion were made using radioactive Fe^{59}. In no instance was any measurable exchange observed. The compound was subjected to neutron irradiation and the Szilard–Chalmers yield of separable activity calculated and identified. The separated portion contained less than 1% of the total activity and consisted of Fe^{59}, P^{32}, and S^{35}.

The lack of exchange and the low Szilard–Chalmers yield are attributed to the formidable steric hindrance effects which result from the "stacked layer" structure for graphite ferric chloride.

INTRODUCTION

It is known that the layers of carbon atoms in graphite can be intercalated with certain elements and compounds (6). The many examples include such varied materials as potassium (2, 5), bromine (7, 5), ferric chloride (7), and, with accompanying oxidation, bisulphate ion (8). In many of these cases a distinction is made between the "lamellar" compound initially formed and the "residue" compound formed from it by heat or solvent action (3). X-ray studies show that in the lamellar complex the layers of carbon atoms are about 8 Å apart as compared with 3.34 Å for graphite, whereas in the residue compounds the separation returns to 3.34 Å. The residual adduct in the latter case is believed to be very strongly held on lattice imperfections (4).

In the case of ferric chloride between 60 and 72% enters the lattice in the range 200 to 309°C. Treatment of these products with acid reduces the amount to 53%, which corresponds closely to $C_{12}FeCl_3$ and leaves a layer separation of 9.4 Å. The residue compound, containing 5% $FeCl_3$, is obtained above 410°C. In the lamellar compound with 53% chloride it is believed that the carbon is bonded to adjacent layers of chlorine atoms, which in turn enclose a layer of iron atoms. Rudorff (7) suggests that there is a polarization of the conductivity electrons of the carbon layers toward the central layer of iron atoms, but that these remain essentially ionic. There will then be electrovalent bonding of the chloride ions to the macro positive ion layer planes. The original purpose of this work was to learn something about these bonds by measuring the exchange of iron between the compound and iron in solution and by measuring the extent of any Szilard–Chalmers reaction on neutron irradiation. The complete lack of exchange, however, means that other methods must be used at least within the time and temperature limits of this work.

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Contribution from the Department of Chemistry, University of British Columbia, Vancouver, B.C., with financial assistance from the National Research Council of Canada.
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EXPERIMENTAL

1. *Preparation of Materials*

(*a*) *Ferric Chloride Anhydrous*

Dry chlorine was passed over c.p. iron powder at 350°C. in a glass tube until no more hexagonal platelets of a deep red wine color formed in the cool portion of the tube. The crystals were cooled in a stream of dry air and removed and handled only in a dry box. The active chloride was prepared by using radioactive iron wire with the powder.

(*b*) *Graphite Ferric Chloride,* $C_{12}FeCl_3$

Acid purified, 200-mesh graphite (G66 of Fisher Scientific Co.) was mixed with three times its weight of anhydrous ferric chloride, sealed in a Carius bomb tube, and heated for 12 hr. at 305°C. The excess ferric chloride was removed by three successive 12 hr. refluxings with boiling 6 *N* HCl.

2. *Analysis of the Graphite Ferric Chloride*

(*a*) *Acid-soluble Ferric Chloride*

Five grams of purified product were further refluxed with acid for six hours. The extract, evaporated to 1/10 of its volume, gave no color with ammonium thiocyanate solution. From the known sensitivity of this test, there must have been less than 10 μgm. of ferric ion extracted per gm. of graphite ferric chloride.

A second test was made on purified $C_{12}FeCl_3$ containing 2.3×10^5 counts of Fe^{59} per min. per gm. The extract prepared as above and counted showed less than 4 μgm. of ferric ion extracted per gm. of $C_{12}FeCl_3$.

(*b*) *Gravimetric Analysis*

From the original weight of graphite and the final weight of purified compound for eight preparations, a figure of $53.04 \pm 0.09\%$ $FeCl_3$ was obtained. This gives a ratio of $FeCl_3$ to C of 1 to 11.96 ± 0.03.

(*c*) *X-ray Analysis*

These measurements were made on both graphite and $C_{12}FeCl_3$ with a Phillips Geiger-Counter X-ray Spectrometer using the 1.539 Å Cu line. Fig. 1 is a plot of intensity against glancing angle, which is θ in the equation $n\lambda = 2d \sin\theta$. Table I lists the values for graphite ferric chloride. The first

TABLE I

THE PRINCIPAL DIFFRACTION LINES OF GRAPHITE FERRIC CHLORIDE POWDER

2θ, degrees	d, Å	I/I_{max}
8.1	10.90	0.30
9.4	9.40	0.64
11.8	7.49	0.25
19.0	4.66	1.00
26.8	3.32	0.21
28.5	3.13	0.81
52.2	1.42	0.11
58.8	1.57	0.10
68.1	1.37	0.12

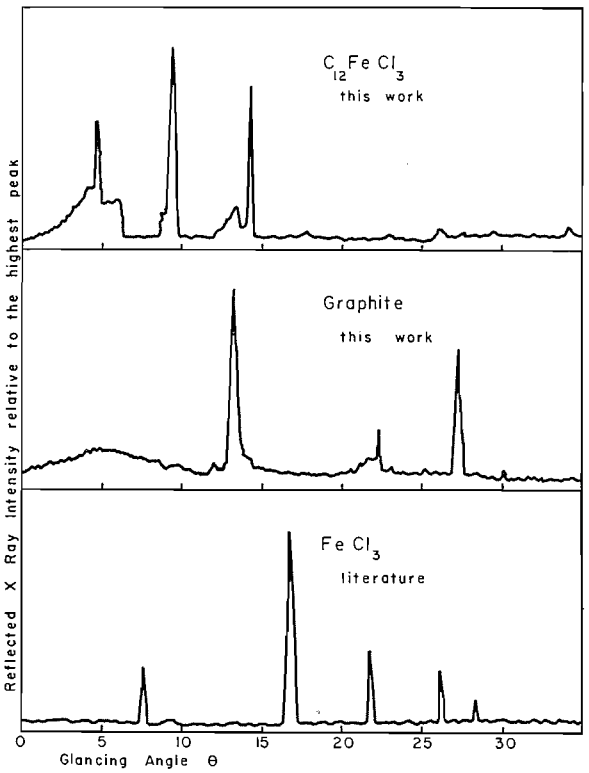

FIG. 1. The reflection of X rays from a powder.

peak for this compound gives a value of $d = 9.40$ Å and is interpreted as the distance between carbon layers. The first peak for graphite at 13.2° corresponds to the layer-plane separation of 3.36 Å. The literature values are 9.4 Å for $C_{12}FeCl_3$ (7) and 3.41 Å for graphite (1). For comparison the plot for $FeCl_3$ as taken from the literature (1) is included.

3. Preparation and Measurement of Radioactive Iron

Pure iron wire was activated in the Canadian Atomic Energy Project reactor. A mixture of 47 day Fe^{59} emitting beta and gamma rays and four year Fe^{55} emitting weak X rays was received with an activity of 0.06 mc. of Fe^{59} per gm. and 0.3 mc. of Fe^{55} per gm. The decay curve over a five-month period was linear with a half life of 47 days. This shows that the weak X rays from Fe^{55} were not detected and that for correction of activities to zero time, a half life of 47 days can be used.

Measurements were made with a self quenching counter with a 3 mgm. per cm.^{2} window and a 150 volt plateau. It was shielded to a background count of 42 per minute. The pulses were counted by a Nuclear Instrument Company Model 163 scaling unit.

The solid graphite ferric chloride samples were always less than 0.2 mgm. cm.$^{-2}$ and were therefore not corrected for self absorption. Uniform samples

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of this thickness were prepared as follows: About 20 mgm. of finely divided powder was accurately weighed and slurried with water. This was slowly added to a Buchner funnel full of water and containing a 6 cm. diameter filter paper under slight suction. After the water had run through, four or five circles of damp, sample covered paper were cut at random with a 1.6 cm. diameter cork borer. These were dried in a desiccator and then counted. The over-all spread was never over 5% and the average count was used.

The activities of the evaporated ferric chloride solutions were corrected for self absorption by extrapolating the activities per unit volume of aliquots of 0.2, 0.4, 0.6, and 0.8 ml. to zero volume.

EXCHANGE OF IRON BETWEEN $C_{12}FeCl_3$ AND FERRIC CHLORIDE

An 0.01 to 0.15 gm. sample of $C_{12}FeCl_3$ was mechanically shaken with 5 ml. of 0.05 to 0.50 *M* $FeCl_3$ solution and centrifuged. The specific activities of the washed solid and of the solution were determined. These were corrected for background, decay, and, in the case of the evaporated solution, for self absorption.

In the first set of experiments the graphite ferric chloride had an activity of 1255 ± 10 c.p.m. per mgm. of iron. For times up to four months at 20°C. and a pH of 5 this activity remained the same and the solution acquired none. The same result was obtained in eight hours at 80°C. and in five other solvents. These were acetone, diethyl ether, isopropyl ether, ethanol, and benzyl alcohol at 20°C. for four days and the latter two at 50° and 190° respectively for four hours.

In the second set, the activity was in water solution to the extent of 580 c.p.m. per mgm. of iron. For times up to four months at 20°C. and a pH of 1.0 none of this was transferred to the solid.

THE SZILARD–CHALMERS REACTION IN GRAPHITE FERRIC CHLORIDE

A 1.50 gm. sample of purified $C_{12}FeCl_3$ was irradiated for 48 hr. in a neutron flux of 4×10^{12} per cm.^{2} per sec. in the Canadian Atomic Energy Project reactor at Chalk River, Ontario. The acid extract was separated into its components and the activities of these and that of the solid were studied by measuring the absorption characteristics of their radiations.

1. Separation of the Components

The known products of the irradiation are listed in Table II along with the calculated activity of each component. The amounts of Cl^{36} and Cl^{38} are negligible and the Fe^{55} radiation is not detected by our counter. This leaves only Fe^{59}, S^{35}, and P^{32} as measurable components. These were separated in the extract according to the following method which is similar to one used by Wilk (9).

An 0.100 gm. sample of irradiated $C_{12}FeCl_3$ was refluxed with 200 ml. of 6 *N* hydrochloric acid for six hours and centrifuged. To the aqueous layer was added a few drops of 30% hydrogen peroxide to ensure oxidation to ferric ion. The colorless solution was then shaken with successive quarter volumes of

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TABLE II

THE 48 HR. IRRADIATION OF 1.5 GM. OF GRAPHITE FERRIC CHLORIDE IN A NEUTRON FLUX OF 3.5×10^{12} CM.$^{-2}$ SEC.$^{-1}$

Isotope	Half life	Radiation in Mev.	Range in mgm. cm.$^{-2}$	Calculated activity in mc./gm. of compound 12 hr. after activation
Fe^{55}	3.0 yr.	γ 0.07		0.02
Fe^{59}	45.5 days	β 0.26, 0.46 γ 1.10, 1.30	70, 150	0.005
P^{32}	14.30 days	β 1.7	770	0.01
S^{35}	87.1 days	β 0.17	30	1.3
Cl^{36}	4×10^5 yr.	β 0.66	250	0.0002
Cl^{38}	38 min.	β and γ		10^{-4}

diethyl ether saturated with hydrochloric acid, and finally washed with an equal volume of the solvent. The ether extracts were combined and stripped with distilled water. The activities of the resultant solutions were measured and the components differentiated by absorption measurements to show that the activities present corresponded to those shown in Table II.

Figs. 2 and 3 give these absorption curves and show that most of the

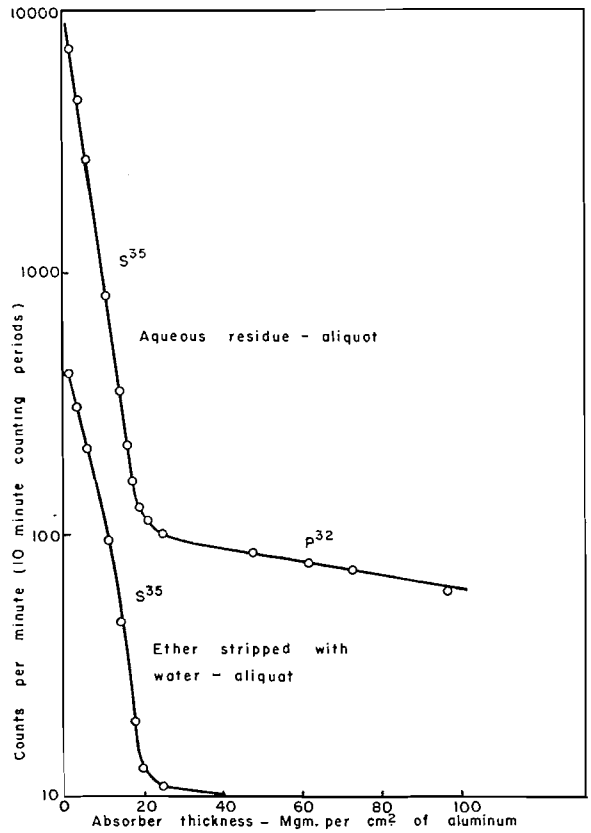

FIG. 2. The absorption characteristics of the separated S^{35} and P^{32}.

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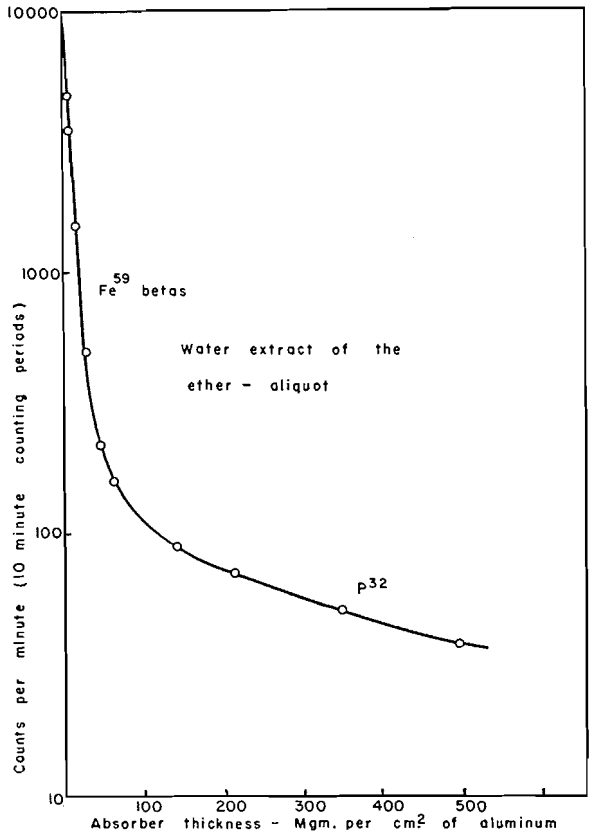

FIG. 3. The absorption characteristics of the separated Fe^{59} and P^{32}.

S^{35} and P^{32} remained in the original aqueous acid extract and that all the iron was transferred to the ether layer and from there to the water extract of that layer.

2. Total Activities of the Original Extract and the Solid

The conditions of time and temperature of extraction were varied and in three extractions the solid was ground with the acid. The results are presented in Table III. They show that 6 *N* hydrochloric acid extracts $0.683 \pm 0.010\%$ of the total activity, whether at 80° or 100°C. and whether for 15 min. or 16 hr. They also show that grinding the solid raises this value to $0.730 \pm 0.007\%$.

The absorption characteristics of the radiations were measured and are shown in Fig. 4. They are the same for the extracted solid and for the acid extract. Both of these, however, show less weak components than does the irradiated compound before extraction. Perhaps the latter process volatilized some of the weakest component, S^{35}. In any case, the over-all process removed the same percentage of each of the three radioactive components.

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TABLE III

THE ACID EXTRACTION OF IRRADIATED GRAPHITE FERRIC CHLORIDE

Conditions	Initial activity in c.p.m. $\times 10^{-5}$	Total separated activity in c.p.m. $\times 10^{-3}$	% extracted
1. 4 *N* HCl at 80°C. stirred 15 min.	58.11±0.11	39.6±1.9	0.681±0.033
2. 6 *N* HCl at 100°C. refluxed 4 hr.	134.32±0.26	92.4±1.7	0.688±0.013
3. 6 *N* HCl at 100°C. refluxed 8 hr.	120.0±0.23	82.0±1.6	0.683±0.013
4. 6 *N* HCl at 100°C. refluxed 16 hr.	87.06±0.16	59.4±1.2	0.682±0.014
5. 6 *N* HCl at 25°C. ground in a mortar for 1 hr.	38.56±0.10	28.08±0.16	0.728±0.004
6. 6 *N* HCl at 100°C. ground between two ground-glass plates before extraction	11.99±0.03	8.7±0.17	0.726±0.014
7. 6 *N* HCl at 100°C. as in "6" but with fine Al_2O_3 grinding powder	13.187±0.04	9.72±0.19	0.737±0.015
Average for non-ground samples 1 to 4			0.683±0.010
Average for ground samples 5 to 7			0.730±0.007

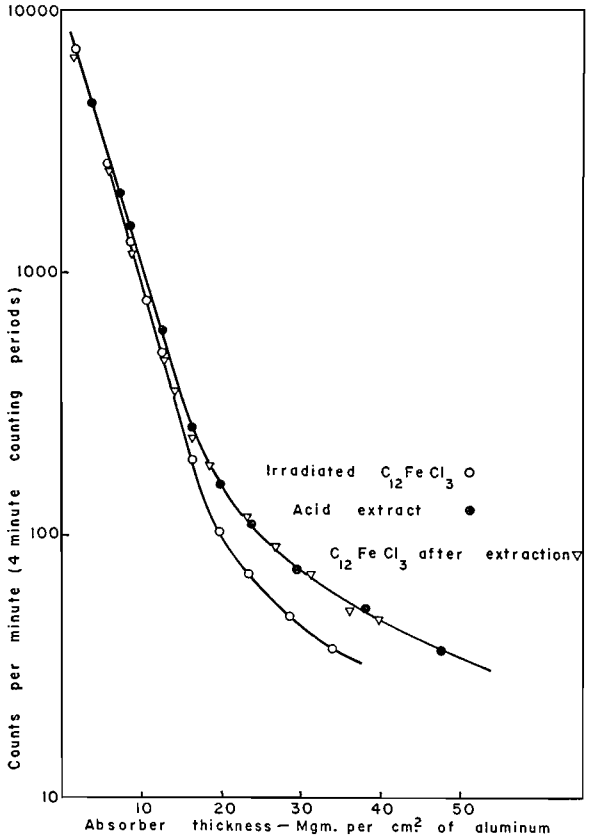

FIG. 4. The absorption characteristics of the irradiated $C_{12}FeCl_3$.

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DISCUSSION

The extraction of activity from neutron irradiated $C_{12}FeCl_3$ could be explained by the initial presence of free ferric chloride. It has been shown, however, that the purified compound contains less than 4 μgm. of Fe per gm. as free chloride. This could account for only 0.3% of the separated activity. The ferric chloride must therefore be bonded to the graphite and bonded in such a fashion as to prevent exchange of iron with a surrounding solution under the attained conditions. Activation of an iron atom with neutrons, however, breaks the bond. The fact that only 1% of the total iron atoms so activated was extractable shows that the remaining 99% recombined with the lattice on dissipation of the energy or/and was not in a position to be reached by the acid. The latter is probably true for the sulphur and phosphorus produced from the chlorine because no stable way of fitting them into the lattice is known, and yet only 1% of them was extracted by acid. It is therefore assumed that the extracted activities came only from the surface layers of the crystal. Grinding would expose fresh surfaces and thereby increase the per cent of extractable activity just as was observed.

ACKNOWLEDGMENT

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ATTEMPTED DELIGNIFICATIONS WITH SODIUM BICARBONATE - CARBON DIOXIDE, AND WITH ANHYDROUS LIQUID AMMONIA, UNDER PRESSURE[1]

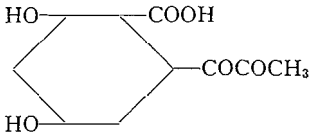
By M. M. Yan[2] and C. B. Purves

ABSTRACT

Finely divided spruce wood was heated with aqueous sodium bicarbonate and excess carbon dioxide up to 160° and about 400 p.s.i. in attempts to carboxylate the lignin according to the Kolbe–Schmitt method and to extract the product as a soluble sodium salt. Only small amounts of lignin were removed, together with larger amounts of the holocellulose. Heating the wood with anhydrous liquid ammonia up to 100° and about 900 p.s.i. extracted only small amounts of material from the softwood spruce, but 25 to 30% of the lignin was removed from the hard woods beech, birch, and maple and 52% from rye straw. The solution of ammonium chloride or sodium cyanide in the liquid ammonia increased these percentages substantially, and also the concomitant extraction of holocellulose.

INTRODUCTION

In an interesting article published in 1943, Kulka and Hibbert (15) pointed out that the oxygenated phenyl propane derivatives resulting from the ethanolysis of wood lignins bore some similarity to the compounds I and II isolated by Oxford and Raistrick (16) from certain strains of *Penicillium brevi-compactum* grown on glucose. The similarity was close in the side chains,



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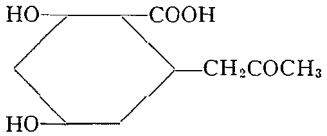

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but the products from lignin differed in being based on vanillin and syringyl units, which were phenolic methyl ethers as well as free phenols, and also in having no carboxylic acid groups. The latter difference was attributed by Kulka and Hibbert to the carboxylation of the non-acidic precursors of I and II by a biochemical process analogous to the well-known Kolbe–Schmitt reaction, in which a phenol was carboxylated by carbon dioxide. In a typical Kolbe–Schmitt synthesis, a mixture of the phenol with anhydrous sodium or potassium carbonate, or the dry sodium or potassium phenolate, was treated at an elevated temperature with carbon dioxide under pressure (6). The carboxyl group entered ortho, or more rarely, para, to the phenolic hydroxyl group, and the yields were generally good. The synthesis, however, proceeded

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with remarkable ease with polyhydric phenols; phloroglucinol when dissolved in glycerol with potassium bicarbonate was carboxylated to a considerable degree even at room temperature (4), and resorcinol required to be warmed with aqueous potassium bicarbonate for only a short time (2). Although lignin *in situ* contained few, if any, free phenolic groups, they were known to be produced in several reactions such as ethanolysis. If this occurred in the conditions of the Kolbe–Schmitt synthesis, the lignin might also acquire carboxyl groups, and be removed from the wood as a water-soluble sodium salt. The present research was designed to explore this possibility.

Approximately equal weights of solvent-extracted spruce wood meal, solid sodium bicarbonate, and solid carbon dioxide were sealed with 20 parts of distilled water in a suitable autoclave, which was then heated for 20–24 hr. as described in Table I. The yield of the residual, undissolved meal and its

TABLE I

KOLBE–SCHMITT COOKS WITH SPRUCE WOOD MEAL[a]

Cook No.	Ratio to wt. of wood[b]		Conditions			Wood residue		Extracted	
	CO_2	$NaHCO_3$	°C.	Hr.	P.s.i.	Yield, %	Lignin,[c] %	Lignin,[d] %	Holocellulose,[e] %
1	1.0	1.0	100	20	265	~100	26.5	—	—
2	0.7	1.0	158	24	215	83.4	29.1	−0.6	<17
3	1.0	1.0	163	24	400	76.7	26.2	2.3	21
4	0	0	163	24	0	75.5	30.9	−2.4	<25
5	0	0	159	24	0	75.1	31.4	−2.9	<25

[a]*Klason lignin, 28.5; methoxyl, 4.7%. All percentages based on original oven-dry wood.*
[b]*To one part of wood and 20 parts of water.*
[c]*Analytical figures multiplied by yield %/100.*
[d]*Data in preceding column subtracted from 28.5% (footnote "a").*
[e]*Calc. as 100 minus (residual yield and extracted lignin).*

Klason lignin content made it possible to calculate the approximate percentage of the original wood that had been extracted as lignin, and, by difference, the amount extracted as non-lignin or holocellulose. The first cook (experiment 1) showed that very little material was removed at 100°. At 158–163°, the extraction of lignin was also negligible, and sometimes small negative values suggested that Klason lignin had been manufactured from other substances in the wood (cook 2). Corey, Calhoun, and Maass (8) found that the apparent Klason lignin content of spruce wood heated in water buffered to pH 3 for 96 hr. at 140° increased from 26.3% to 28.6%, and Aronovsky (1) made a similar observation with pine (another softwood) heated in water at 170°. These observations were confirmed in cooks 4 and 5, in which water alone was used. The low extraction of Klason lignin in the Kolbe–Schmitt cooks and the high extraction of holocellulose (right hand column) made it probable that the sodium bicarbonate–carbon dioxide system served only as a buffer which slightly reduced the hydrolytic action of water (14) on the wood polysaccharides.

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Since the failure of the Kolbe reaction in the above experiments might have originated in a lack of free phenolic hydroxyl groups in the lignin, later trials were carried out on wood samples that had been pretreated with acids or alkalis. The conditions of these pretreatments (Table II) were expected to

TABLE II

KOLBE COOKS WITH PRETREATED SPRUCE MEAL[a]

Cook No.	Pretreatment			Kolbe cooks[b]	Wood residue		Extracted	
	Medium	Hr.	°C.		Yield, %	Lignin,[c] %	Lignin,[d] %	Holocellulose,[e] %
6	H_2O	24	162		75.3	31.2	−2.7	<25
				Cook[f]	72.9	30.0	−1.5	<27
7	0.5% HCl	4	130		67.8	25.2	3.3	29
				Cook	52.6	25.6	2.9	45
8	0.5% HCl	2	100		81.6	26.9	1.6	17
				Cook	59.8	25.6	2.9	37
9	0.5% HCl	2	100		80.0	26.8	1.7	18
				Cook	63.8	27.0	1.5	35
10	1% NaOH	3	100		84.9	26.3	2.2	13
				Cook	74.9	24.6	3.9	21
11	Meal–NaOH[g] (dried)	—	—	Cook[g]	68.4	24.4	5.0	27

[a]*Klason lignin, 28.5%. All percentages based on weight of original oven-dry wood.*
[b]*Water: wood: CO_2: $NaHCO_3$ = 20: 1: 1: 1 by weight; cooks at 158–160° for 24 hr. at about 400 p.s.i.*
[c]*Analytical figures multiplied by yield %/100.*
[d]*Data in preceding column subtracted from 28.5% (footnote "a").*
[e]*Calc. as 100 minus (residual yield and extracted lignin).*
[f]*At 100°.*
[g]*One part NaOH and two parts wood meal dried over P_2O_5 near 20°. Klason lignin 29.4%. Cooked in CO_2 at 400 p.s.i. for 65 hr.*

liberate more free phenolic groups in the lignin by hydrolysis or saponification, but neither the pretreatments nor the subsequent Kolbe–Schmitt cooks removed substantial quantities of the lignin. Cook 6 showed that the process at 100° had a negligible effect on wood pretreated in water at 162°, just as it had on the original wood (Table I, cook 1). The Kolbe–Schmitt cook, however, did extract a substantial additional amount of holocellulose from the samples prehydrolyzed with boiling aqueous acid, perhaps because of the superior solvent action of a slightly alkaline system on partly degraded hemicelluloses (Table II, cooks 7–9). The same effect was noticeable to a lesser degree when the pretreatment was with boiling alkali (cook 10). Since the Kolbe–Schmitt reaction often proceeded better when carried out in the absence of water, the last experiment involved the action of carbon dioxide under pressure on wood meal which had been impregnated with sodium hydroxide and dried to constant weight. A subsequent extraction with warm water removed little lignin, but much of the holocellulose.

The possibility existed that the carbohydrate content of the wood was

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interfering in some way with the response of the lignin to the carboxylating agent. An isolated spruce periodate lignin (17) was accordingly cooked with aqueous sodium bicarbonate – carbon dioxide at 160° and near 400 p.s.i. for 24 hr., but only 22% went into solution. Isolated maple ethanol lignin (3) dissolved to the extent of only 10% in a similar cook at 100°, whereas 13.4% became soluble when a sample was boiled in water for 24 hr. In both cases the light-colored, powdery, ethanol lignin was changed to a very dark, hard, coal-like state. These experiments made it clear that the failure of the Kolbe–Schmitt reaction to remove substantial quantities of lignin could not be attributed to the presence of the wood polysaccharides, but was inherent in the lignin itself. It was probable that resinification caused by the temperature and alkalinity (5) kept the bulk of the lignin insoluble and any carboxylation that occurred had a negligible effect in promoting solubility.

The decision to investigate the action of anhydrous liquid ammonia on woods was based on the facts that it was neither an acidic nor an alkaline reagent, was a much better solvent than water for many organic substances, and differed from water in its capacity to penetrate and swell the crystalline as well as the amorphous portions of cellulose (9). These properties suggested that anhydrous liquid ammonia under pressure might extract much of the lignin and hemicellulose from woods with little chemical change beyond the ammonolysis of any ester linkages present. Freudenberg and his collaborators (11, 12) studied the action on several lignins and woods of solutions of alkali metals and amides in liquid ammonia. An isolated spruce lignin, when treated for 24 hr. at 20° in this way with potassium or potassium amide, was rendered completely soluble in the strongly alkaline solution produced by removing the ammonia and adding water; in similar circumstances 50% of spruce wood meal dissolved, and the soluble portion included two-thirds of the lignin. Later investigations of the same type were described in a series of articles by Shorygina and co-workers (18). Extensive chemical change, including demethylation of the lignin, was involved in these reactions, doubtless because in liquid ammonia an alkali metal would function as one of the strongest reducing agents known, and an alkali metal amide would be a strong base (10).

In the present work, the weight ratio of anhydrous liquid ammonia to the oven-dry weight of the wood meal was 15 : 1, but the meal was added in an air-dry condition containing about 7% of moisture. The concentration of water in the system was thereby increased from about 0.03% to about 0.5%. Control experiments made with maple wood and rye straw meals which had been thoroughly dried over phosphorus pentoxide showed, however, that such drying increased the amount extracted by less than 1%. Special care was taken to eliminate the access of adventitious moisture while the ammonia was removed at the end of the extraction. The yield of undissolved wood and its Klason lignin content furnished the approximate amounts of holocellulose and lignin extracted. Unlike the results of the Kolbe–Schmitt cooks, the latter amounts were never negative.

As the data of Table III show, anhydrous liquid ammonia extracted only 9% of the Klason lignin from spruce wood even at 100°, or at a temperature

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TABLE III

EXTRACTION OF WOODS AND STRAW WITH LIQUID AMMONIA[a]

Expt. No.	Conditions[b] °C.	Conditions[b] Hr.	Residual meal Yield, %	Residual meal Lignin, %	Extracted Lignin, %	Extracted Holocellulose, %	Per cent of lignin extracted
Spruce with 28.5% lignin							
1	25	16	97.0	—	←3→		—
2	45	44	—	28.4	—	—	—
3	100	65	96.8	25.9	2.6	0.6	9
Birch with 19.2% lignin							
4	75	40	88.0	15.2	4.0	8.0	21
5	100	3	91.7	16.3	2.9	5.4	15
6	100	65	85.7	12.8[c]	5.5	8.8	30
Beech with 22.7% lignin							
7	75	40	90.7	18.7	4.0	5.3	18
8	100	24	89.5	17.2	5.5	5.0	24
Maple with 21.4% lignin							
9	75	40	89.6	16.8	4.6	5.8	22
10	100	24	88.4	16.1	5.3	6.3	25
Rye straw with 19.7% lignin[d]							
11	100	65	80.1	9.7	10.0	9.9	51
12[e]	100	24	76.5	9.5	10.2	13.3	52
13[e]	100	3	81.6	9.5	10.2	8.2	52
14[e]	25	65	88.6	13.3	6.4	5.0	33

[a]*Air-dry samples. Calculations as in footnotes to Tables I and II.*
[b]*Ratio of liquid NH_3 to bone-dry sample, 15: 1 by weight.*
[c]*Original birch had 18.3% lignin.*
[d]*Data corrected for ash in straw (6.46%) and in Klason lignin.*
[e]*Total moisture in system less than 0.1%.*

fairly close to the critical temperature of 133° recorded for this solvent. Extraction of birch, beech, and maple samples at 100° for 24 to 65 hr., however, removed 24 to 30% of all the lignin present, and the amount increased to just over 50% with the rye straw. The low response of the softwood, spruce, as compared to those of the three hardwoods, was in agreement with the general behavior of the two classes of wood toward other methods of extraction (14), and the still greater response of the rye straw was also to be expected. Comparison of experiments 1 and 3; 7 and 8, and 9 and 10; and 13 and 14 showed that an increase in temperature produced an insignificant change in the amount of material extracted by the liquid ammonia from spruce, a moderate increase in the amounts from the hardwoods, and a major increase in the amount from the rye straw.

In all the experiments described in Table III, the ammonia cellulose, if produced in wood as in cellulose itself, would be of type I (9). A type II ammonia cellulose with a greatly expanded unit cell was known to exist below −30°, and Clark and Parker (7) found that in these conditions cellulose fibers were swollen to three times their original diameters. It seemed desirable to carry out some extractions at less than this temperature. Air-dry spruce and rye straw meals were accordingly extracted with anhydrous liquid ammonia at its boiling point of −33° for 200 hr., but the losses in weight were negligible,

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even in the case of the straw. Black spruce chips, however, increased in volume by only 6% when soaked in liquid ammonia at −33° for 22 hr., and it was concluded that the presence of the lignin prevented much swelling of the cellulose. These swollen chips contracted to slightly less than their original volume when the ammonia was allowed to evaporate in the air. Similar but more detailed experiments were made on other woods by Stamm (19), who also noted that the amounts extracted by liquid ammonia near −33°, and by hot water, were about the same.

Although anhydrous liquid ammonia by itself had only a limited extractive action on lignin *in situ*, it seemed possible that solutions of certain salts might be more effective, since in the ammonia system salts like ammonium chloride were known to be ionized and to function as acids (10). Table IV summarizes

TABLE IV

EXTRACTIONS WITH VARIOUS SALTS IN LIQUID AMMONIA[a]

Expt. No.	Salt[b]	Residual meal		Extracted		Per cent of lignin extracted
		Yield, %	Lignin, %	Lignin, %	Holocellulose, %	
Spruce with 28.5% lignin						
15	NH_4Cl	88.0	24.6	3.9	8.1	14
16	NH_4Cl	87.3	23.9	4.6	8.1	16
17	$(NH_4)_2SO_3$	97.0	25.7	2.8	0.2	10
18	$(NH_4)_2SO_4$	96.4	27.0	1.5	2.1	5
19	NaCN[c]	75.3	23.6	4.9	19.8	17
Birch with 18.3% lignin						
20	NH_4Cl	77.3	11.1	7.2	15.5	39
21	$(NH_4)_2SO_3$	79.6	11.5	6.8	13.6	37
Rye straw with 19.7% lignin[d]						
22	NH_4Cl	79.1	8.2	11.5	9.4	58

[a] *Meal samples air-dry. Calculations as in footnotes to Tables I and II.*
[b] *Ratio of liquid ammonia to bone-dry sample to salt, 15 : 1 : 0.75 by weight. All mixtures heated at 100° for 65 hr.*
[c] *Ratio of liquid ammonia to bone-dry sample to salt, 15: 1: 4.5 by weight.*
[d] *Data corrected for ash in straw (6.46%) and in Klason lignin.*

some relevant experiments, made at 100° for 65 hr. with 4.5% solutions. Of the added ammonium salts, the chloride had the most pronounced action, and raised the amount of lignin extracted from 9% to about 15% in the case of spruce (Table III, expt. 3, and Table IV, expts. 15, 16), from 30% to 39% for birch, and from about 50% to 58% for the rye straw. The extraction of holocellulose from the two woods, but not from the straw, was also substantially increased. Ammonium sulphite in liquid ammonia, which was considered to be the nearest equivalent to the sulphite cook in the aqueous system, was of negligible advantage for spruce, but was almost as good as was ammonium chloride for birch (Table IV, expts. 17 and 21). The extraction of 37% of the lignin probably did not involve sulphonation, because no sulphonic acid groups could be detected in the birch wood residue by the color test employing *p,p'*-azodimethylaniline in acetic acid (13). The addition of ammonium sulphate was of no value (expt. 18), but this salt, like the sulphite, was reported

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to be almost insoluble in liquid ammonia. Since sodium cyanide was very soluble, it was possible to use a 23%, instead of a 4.5%, solution, and no less than 17% of the lignin in spruce wood was extracted (expt. 19). Sodium cyanide was presumably non-acidic in liquid ammonia, and its pronounced solvent action on both the lignin and the hemicellulose was unexpected.

Although only minor portions of the wood lignins had been extracted in the experiments just described, the liquid ammonia might have promoted physical or chemical changes which rendered the residual lignin extractable by other reagents. To test this possibility, the spruce and birch wood residues from extractions using liquid ammonia alone, and ammonia containing ammonium chloride or sulphite, were boiled for two hours with 1% aqueous sodium hydroxide. The additional amount of lignin extracted ranged from 2.2% to 8.7% of that in the original wood, but this small loss was usually accompanied by a much greater additional loss of holocellulose.

EXPERIMENTAL

Materials and Analytical Methods

All the wood meals and the rye straw were exhaustively extracted first with alcohol–benzene, then with alcohol, and finally with hot water. After being dried in the air, the meals were used in mesh sizes 20–100 for the rye straw, 40–100 for the spruce, and 60–80 for the beech, birch, and maple samples. The commercial liquid ammonia was claimed to be of 99.95% purity and to contain only 0.03% of water.

Klason lignin determinations were carried out in duplicate on 0.1 gm. to 0.6 gm. samples by scaling down the standard T.A.P.P.I. method (20); all results were corrected for moisture content, and also for ash when the latter was considerable, as it was for the rye straw.

Cooks with Sodium Bicarbonate – Carbon Dioxide (Tables I and II)

A stainless steel bomb of 130 cc. capacity and with walls 12 mm. thick was fitted with a stout, stainless steel lid with a lead gasket. Closure was effected by a bolt which pressed against the top of the lid. The other end of the bolt was anchored into a heavy cap, the inner part of which engaged a screw threaded on the outside of the bomb.

The bomb was loaded with 90 cc. of distilled water, 4.5 gm. of sodium bicarbonate, and an equal weight of the air-dry wood meal. Carbon dioxide was bubbled through the solution to remove air, 4.5 gm. of solid carbon dioxide was quickly added, and the bomb sealed. This weight of carbon dioxide gave a pressure of about 400 p.s.i. at 160°. The bomb was heated either in a steam bath at 100°, or in a thermostatically controlled oil bath, for the prescribed time and was then cooled in water. After the pressure had been carefully released the wood meal was removed, thoroughly washed with water, and dried in the air.

Prior to being cooked, some wood samples, 7.5 gm., were extracted by 150 cc. of aqueous acid or alkali (Table II). Hydrolyses at 100° were carried out under reflux at atmospheric pressure, but a stainless steel bomb of 280 cc. capacity (see below) was used when the temperature was higher. One wood sample was

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soaked in 17.5% aqueous sodium hydroxide for one hour at room temperature in a nitrogen atmosphere. After being recovered by filtration and pressing, the meal was dried for several weeks *in vacuo* over phosphorus pentoxide. The dry, yellow product contained 29.4% of Klason lignin, after correction for 33% of sodium hydroxide.

Cooks with Anhydrous Liquid Ammonia (Tables III and IV)

The vapor pressure of liquid ammonia at 100° was about 910 p.s.i. and it was necessary to employ the thick-walled bomb just described. The lid was replaced with a rubber stopper through which a glass inlet tube just passed, and through which a glass exit tube projected. This projection ended just above a level in the bomb corresponding to a volume of 70 cc., equivalent to 50 gm. of ammonia at −60°. After being weighed, the assembly was thoroughly chilled to about −60° in a bath of acetone containing solid carbon dioxide, and liquid ammonia was added from a cylinder until liquid was seen in the exit tube. The assembly was then disconnected and quickly reweighed to make sure that 50±1 gm. of liquid ammonia had actually been added.

A weight of air-dry wood corresponding to 3.33 gm. oven-dried, plus 2.5 gm. of the particular salt present in some experiments, was chilled to −60° in a wide-mouthed weighing bottle and was quickly added to the liquid ammonia in the bomb. If this chilling was inadequate, a violent evolution of ammonia gas scattered the meal. The bomb was then securely sealed with its lid and screw cap before atmospheric moisture had a chance to freeze on the threaded surface. Not more than 20 min. was required for the entire filling operation. When the oil bath was used to heat the bomb, care was taken to keep oil away from the threaded portion, and, when steam was used, all moisture had to be removed from this portion by subsequent heating for 30 min. in an air bath at 100°. Neglect of this precaution made it very difficult to open the bomb after it had been thoroughly chilled, first to −15°, and then to −60°, because ice had formed in the threads.

The open bomb, still kept at −60°, was quickly closed with a rubber stopper carrying an inlet tube for dry nitrogen gas or liquid ammonia, an exit tube for gaseous ammonia terminating just below the stopper, and another exit tube for wood meal and liquid ammonia terminating just above the bottom of the bomb. The two exit tubes, each with a stopcock of bore large enough to create no obstruction, led through a rubber stopper into a sintered glass filter crucible. This stopper was also pierced by a safety tube whose outer end was protected from atmospheric moisture by a guard tube containing pellets of sodium hydroxide. A Buchner suction filter flask received the effluent from the crucible. This assembly permitted the contents of the bomb to be transferred to the filter near −60°, and the wood meal to be washed about six times with fresh liquid ammonia, all without access of air or moisture. When the washing was complete, the bomb was allowed to attain room temperature, a stream of nitrogen meanwhile being maintained to assist in the evaporation of the ammonia. Any of the dry wood meal remaining in the bomb was then transferred to the filter and the last traces of ammonia were removed by passing dry air through the assembly for 12 hr. When a salt had been added to the cook, the

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ammonia-free wood meal was thoroughly extracted with warm water and was again air-dried.

In several experiments, the liquid ammonia filtrate was evaporated (with exclusion of moisture) to a light brown, transparent, brittle resin which was dried to constant weight over phosphorus pentoxide. Since this weight was usually very slightly higher than the loss in weight the wood meal incurred in the cook, it seemed probable that the products included combined ammonia. Crystals of acetamide, indeed, occasionally separated from the extract.

A second stainless steel bomb, of lighter construction and of 280 cc. capacity, was sometimes used in liquid ammonia cooks at 45° or less. The lid of this bomb was provided with a $\frac{1}{8}$ in. needle valve for introducing the ammonia, and with an ammonia pressure gauge reading up to 300 p.s.i. This bomb was also used to carry out cooks at $-33°$ and atmospheric pressure for long times, the bomb being set in a vacuum jar held in a $-15°$ brine bath, and the needle valve being left open. In these circumstances the evaporation of ammonia was so slow that no replenishment was needed. The swelling of spruce chips in liquid ammonia was investigated in the same way, each chip being carefully measured with dividers and identified with a metal tag. After immersion for 22 hr., the chips were removed and quickly measured, allowed to stand for another 22 hr. in the air, and measured again.

ACKNOWLEDGMENTS

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A REDETERMINATION OF THE RELATIVE ENTHALPIES OF AQUEOUS PERCHLORIC ACID SOLUTIONS FROM 1 TO 24 MOLAL[1]

By D. R. Bidinosti[2] and W. J. Biermann

ABSTRACT

Previous tabulations of enthalpies of formation of perchloric acid solutions are not in agreement with the behavior expected for an acid as highly dissociated as perchloric acid. Measurements of the heats of neutralization of perchloric acid solutions with sodium hydroxide solutions were made and new values of the relative apparent partial molal enthalpies of perchloric acid solutions in the range 1 to 24 molal were computed from these. These new values agree with the anticipated behavior of perchloric acid.

Traditionally, any deviations of strong electrolyte solutions from ideal behavior are explained in terms of interionic attraction, dissociation of structures, and solvation of the ions produced in dissociation. Considering their effects on the heat of dilution, the first two will tend to make the process endothermic, while the third is an exothermic process. Lacking both theoretical and experimental information about the interionic attraction effects in concentrated electrolyte solutions, one can adopt as a working hypothesis the fact that, as a first approximation, for a given electrolyte type, heat of dilution contributions from these effects will be a function only of ionic strength but not of the specific nature of the electrolyte. Specific differences in heats of dilution of strong electrolyte solutions will then be explainable as differences in hydration and degree of dissociation. This view is confirmed by the similarity of the relative enthalpies of solutions of salts of the larger alkali metal ions with large anions (7), where we anticipate little hydration and complete dissociation.

Such a simplified picture is consistent with the tabulated values of the heats of formation of nitric acid solutions (5). Nitric acid is known to be incompletely dissociated even at relatively low concentration (8, 9), so that on dilution an appreciable number of protons are dissociated and upon hydration liberate sufficient energy that the over-all heat of dilution of nitric acid is exothermic at all concentrations appreciably removed from infinite dilution.

Perchloric acid is a much stronger acid than nitric acid. Undissociated perchloric acid can be detected at high concentrations, but below the vicinity of eight molal the concentration of undissociated molecules is too low to be detected (10). At very high concentrations it is to be expected that perchloric acid will resemble nitric acid in showing a substantially exothermic heat of dilution to infinite dilution, but in the vicinity of eight molal, as protons cease to be made available in quantity for the exothermic solvation process, there

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[2]*Holder of a National Research Council Bursary.*

should be a marked tendency for the process to become less exothermic. At lower concentrations it would appear necessary for the heat of dilution of perchloric acid to become markedly endothermic and, in fact, resemble such salts as sodium or potassium chloride, since, once dissociation is complete, thermal effects on dilution must be due almost entirely to interionic attraction.

The tabulated values of the heats of formation of perchloric acid solutions (2, 5) are quite different from this expectation, indicating the process to be exothermic down to about three molal and then to become endothermic by merely a few calories per mole. Because these older values could not be rationalized, they were suspect and a re-examination of the heat of dilution of perchloric acid solutions was indicated.

EXPERIMENTAL

The relative apparent partial molal enthalpies of perchloric acid solutions at various concentrations were determined indirectly by measuring the heat of neutralization of perchloric acid solutions by sodium hydroxide solutions of the same concentrations. The apparatus and technique have been described previously (1, 4).

A stock solution of carbonate free sodium hydroxide was prepared, diluted, and analyzed gravimetrically as in the earlier neutralization work. Reagent grade perchloric acid was used without further attempts at purification, and analyzed by weight titration against a gravimetrically standardized sodium hydroxide solution. Care was taken that the difference in concentration of a given acid–base set was as small as possible because of a lack of the data required to make exactly the small correction for concentration difference. Similarly, all neutralizations were started at a temperature within a few hundredths of a degree of 25.00° C., because there is insufficient heat capacity data to calculate the temperature coefficient of the reaction. In the concentration region studied, the difference in composition of the vapor phase before and after the reaction leads to heat effects of negligible magnitude. The experimental results of the heat of neutralization observations are recorded in Table I.

CALCULATION

The relative apparent partial molal enthalpy of the perchloric acid solution at the molality m, $\Phi_L(HClO_4, m)$, is then related to its heat of neutralization ΔH_N by sodium hydroxide of molality m by the relationship:

$$\Delta H_N = \Delta H_N^\circ + \Phi_L(NaClO_4, m') - \Phi_L(HClO_4, m) - \Phi_L(NaOH_4, m).$$

The molality of the reactants, m, is taken as the average of the closely adjusted acid and base concentrations, and m' is the concentration of the salt solution which results, related to m by

$$m' = 55.51\ m/(111.02 + m)\ .$$

The heat of neutralization at infinite dilution, ΔH_N°, was taken as $-13{,}321$ defined calories per mole (1). The values of the relative apparent partial molal

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TABLE I

EXPERIMENTAL DATA FOR THE HEAT OF NEUTRALIZATION OF PERCHLORIC ACID AND SODIUM HYDROXIDE SOLUTIONS AT VARIOUS MOLALITIES

m ($HClO_4$)	m (NaOH)	ΔH_N, def. cal. 25.0°C.
24.299	24.291	24,086 24,089
20.081	20.099	21,822 21,851
16.083	16.090	19,474 19,476
13.411	13.410	17,824 17,834 17,837
11.233	11.221	16,626 16,627
9.193	9.195	15,633 15,628
7.860	7.856	14,980 14,982
6.080	6.103	14,317 14,301
5.008	5.018	14,032 14,034
4.020	4.014	13,673 13,684
2.524	2.538	13,478 13,485 13,470
1.012	1.011	13,381 13,383 13,401

enthalpies of sodium perchlorate solutions have been determined by Colomina and Nicolas (6). The relative apparent partial molal enthalpies of sodium hydroxide solutions are taken from Bertetti and McCabe (3), whose data were converted to defined calories per mole at 25° C. and corrected for an extrapolational error due to inclusion of Richards and Gucker's (11) low concentration data.

Table II presents smoothed values of the heat of neutralization of sodium hydroxide and perchloric acid solutions at integral concentrations, obtained by applying an approximately fitting analytic function and deviation curve to the original data. Included are the relative apparent partial molal enthalpies of the perchloric acid solutions and the partial molal enthalpy of perchloric acid at integral concentrations, together with the supplementary data used in their computation.

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TABLE II

HEAT OF NEUTRALIZATION OF NaOH WITH $HClO_4$ AT INTEGRAL CONCENTRATIONS, AND ENTHALPIES OF PERCHLORIC ACID SOLUTIONS, AT 25°C. IN DEFINED CALORIES PER MOLE

m (reactant molality)	m product molality	$-\Delta H_N$	$\Phi(NaOH, m)$	$-\Phi(NaClO_4, m)$	$\Phi(HClO_4, m)$	$\Phi_2(HClO_4, m)$
1	0.4955	13,380	82	271	−295	−390
2	0.09823	13,440	8	481	−380	−540
3	1.460	13,510	−21	664	−455	−640
4	1.930	13,675	4	836	−500	−500
5	2.392	13,955	69	985	−420	150
6	2.846	14,280	167	1115	−325	420
7	3.293	14,665	303	1217	−180	765
8	3.731	15,090	474	1316	−25	1150
9	4.163	15,540	677	1412	125	1570
10	4.587	16,010	906	1491	295	2040
11	5.004	16,515	1162	1558	475	2565
12	5.415	17,040	1435	1617	670	3150
13	5.819	17,595	1729	1673	875	3790
14	6.217	18,180	2019	1725	1115	4520
15	6.608	18,785	2319	1774	1370	5325
16	6.993	19,415	2615	1820	1660	6215
17	7.372	20,015	2909	1862	1925	7010
18	7.745	20,605	3194	1902	2190	7085
19	8.113	21,200	3476	1936	2470	7560
20	8.475	21,785	3741	1967	2755	8035
21	8.831	22,290	2995	1995	2975	8435
22	9.182	22,805	4239	2020	3225	8855
23	9.528	23,345	4475	2044	3505	9305
24	9.868	23,920	4696	2062	3840	9795

DISCUSSION

The discrepancy between the Berthelot results and those of the present work is substantial, as shown in the selected values of Table III. We are inclined to

TABLE III

COMPARISON OF THIS WORK WITH THE EARLIER VALUES

Molality	Defined calories per mole	
	Berthelot	This work
2	−20	−380
3	−10	−455
4	5	−500
8	220	−25
9	305	125
15	880	1370

prefer the results of the present work because previous experience with the neutralization measurements, as well as an analysis of contributing errors, indicates that the maximum error in the heat of neutralization values is not apt to be greater than 20 calories per mole. The auxiliary data used in computing the relative apparent partial molal enthalpy of perchloric acid could not account for a significant portion of the discrepancies of Table III.

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The results of this work agree satisfactorily with the anticipated behavior of perchloric acid on dilution, showing a rapid curtailment of the exothermic process in the region where dissociation is known to be effectively complete, and below this region resembling the "strong" salts much more closely than it resembles nitric or other weaker acids in its heat of dilution properties.

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THE REACTION OF TETRAMETHYLTHIURAMDISULPHIDE WITH ACETONE

I. REACTION PRODUCTS[1]

By J. R. Robinson,[2] David Craig,[3] and Ray B. Fowler[3]

ABSTRACT

Tetramethylthiuramdisulphide reacts with acetone to form various dithiocarbamate derivatives of acetone, dimethylamine, and carbon disulphide. The reaction has an induction period which is markedly influenced by various additives. The reaction products, their properties and synthesis, are described.

Tetramethylthiuramdisulphide, "TMTD" or "*bis*-(dimethylthiocarbamoyl)-disulphide", is well known as a vulcanization accelerator and as a potent fungicide. In handling hot acetone solutions of the material we have observed evidence of rapid decomposition; even at room temperature, discoloration occurs in a few hours. A survey of the literature indicates that other workers have noted this instability (4, 5, 7, 8) but no one appears to have reported on the composition of the reaction products. An investigation of the process was considered worth while as it might help to elucidate the chemical behavior of TMTD as an accelerator and a fungicide.

DISCUSSION

We have found that TMTD (I) reacts with refluxing acetone to form 1-(dimethylthiocarbamoylthio)-2-propanone (II), dimethylammonium dimethyldithiocarbamate (IV), dimethylamine, carbon disulphide, 1,3-*bis*-(dimethylthiocarbamoylthio)-2-dimethylamino-1-propene (V), and 1,3-*bis*-(dimethylthiocarbamoylthio)-2-propanone (VI). There was no evidence of a 1,1-isomer of VI, and we were unable to isolate the expected monosubstituted propene, VII. The enamine (V) readily hydrolyzes to the propanone derivative VI.

Several grades of acetone were tried including material purified through the bisulphite compound, "Spectro Grade", "Certified Reagent Grade", and commercial amine-free acetone (Carbide and Carbon Chemical Corporation, C.P. grade). The latter material was used for the experiments reported here, as all grades gave the same products. In paper II of this series (3) (Table I), the effect of water upon the reaction is shown to be relatively small, so no attempt was made to dry the acetone.

On the basis of earlier studies of the TMTD vulcanization of rubber (1, 2) we also expected to find sulphur, tetramethylthiurammonosulphide, dimethyl-

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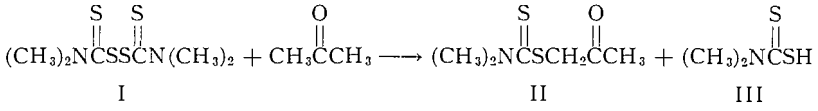
Joint contribution from the Science Service Laboratory, Canada Department of Agriculture, University Sub Post Office, London, Ontario (Publication No. 56A) and the B.F. Goodrich Research Center, Brecksville, Ohio.
[2]*Science Service Laboratory, Canada Department of Agriculture, University Sub Post Office, London, Ontario.*
[3]*The B.F. Goodrich Research Center, Brecksville, Ohio.*

thiocarbamoyldimethylsulphenamide, and tetramethylthiourea; none of these materials was found, nor was acetonylacetone.

We were unable to form the disubstituted compound VI by treating the monosubstituted acetone (II) with excess TMTD in dry benzene; similarly, the reverse attempt to form II by refluxing VI with acetone failed. Attempts to synthesize the propene derivative (V) by treatment of VI with dimethylamine in the presence of dehydrating agents were unsuccessful.



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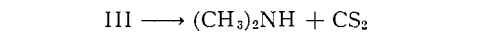

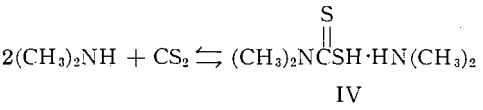

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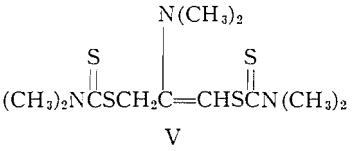

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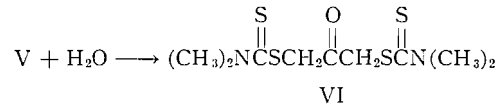

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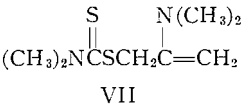

VII

The structures of the mono- and di-substituted acetones (II and VI) were confirmed by synthesis from the appropriate chloro- and bromo-acetones, using the method of Nachmias (6) who reported II but not VI.

The TMTD–acetone reaction exhibits an induction period the length of which can be completely controlled by the use of suitable additives. The most potent activator of the reaction is dimethylamine, or its salt, dimethylammonium dimethyldithiocarbamate (IV). Since most samples of TMTD contain varying amounts of IV as an impurity, different induction periods will be noted with different samples, as the influence of IV is proportional to its concentration. The addition of acetic anhydride, on the other hand, will inhibit the reaction indefinitely. A more detailed study of the influence of additives may be found in paper II of this series.[4]

[4]*See the next paper in this Journal.*

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EXPERIMENTAL

1-(Dimethylthiocarbamoylthio)-2-propanone (II)

A mixture of 24.0 gm. (0.1 mole) of TMTD and 60 ml. of benzene was refluxed for 2.5 hr. during the addition of 6.4 gm. (0.11 mole) of acetone. Refluxing was continued for one hour. The mixture was cooled to 10° and filtered to give 6.6 gm. of dimethylammonium dimethyldithiocarbamate (IV) which melted at 131–135° with decomposition. The filtrate, containing CS_2, was distilled until nearly all the benzene was removed. The addition of ether caused the slow crystallization of Crop 1, 0.5 gm., m.p. 150–152°. The filtrate on evaporation gave 4.5 gm. of solid (Crop 2), which melted at 47–50° and at 58° after crystallization first from water and then from alcohol–water mixture. Anal. Calc. for $C_6H_{11}NOS_2$: C, 40.63; H, 6.26; N, 7.90; S, 36.18%. Found: C, 40.50; H, 6.26; N, 7.89; S, 36.24%.

The compound thus analyzes for 1-(dimethylthiocarbamoylthio)-2-propanone or "acetonyldimethyldithiocarbamate" (II), a compound reported by Nachmias (6) as the reaction product of sodium dimethyldithiocarbamate and monochloracetone. Using his method, we secured II in 90% yield, melting at 58° alone or mixed with the II from Crop 2 above. We have not observed the melting point of 73° reported by him. Dr. A. Quevauviller has forwarded to us a sample of the Nachmias compound. We found it to melt at 58° alone or mixed with our II. The material fails to give the iodoform test. It is soluble in hot water and most organic solvents.

1,3-bis-(Dimethylthiocarbamoylthio)-2-propanone (VI)

The filtrate from Crop 2 (above), on standing, deposited a further 0.6 gm. of crystals melting at 150–152° alone or mixed with Crop 1. Recrystallization from alcohol gave colorless needles, m.p. 158°. Anal. Calc. for $C_9H_{16}N_2OS_4$: C, 36.45; H, 5.43; N, 9.45; S, 43.25%. Found: C, 36.55; H, 5.42; N, 9.34; S, 43.19%.

This compound is quite soluble in benzene, slightly soluble in alcohol, and nearly insoluble in hexane, water, and ether. Samples prepared by the method of Nachmias (6) from 1,3-dihalo-2-propanones melted at 158° alone or mixed with VI from Crop 1 above.

Significantly higher yields of both II and VI were later obtained by eliminating the benzene and simply refluxing an acetone solution of TMTD. After an initial induction period, the same products were formed. The reaction was greatly accelerated (shown by earlier color development, amine and CS_2 formation) by the addition of a crystal of dimethylammonium dimethyldithiocarbamate. The acetone was then evaporated, the products extracted from the residue with appropriate solvents and recrystallized as described above.

1,3-bis-(Dimethylthiocarbamoylthio)-2-dimethylamino-1-propene (V)

In some experiments, difficulty was encountered in separating II from VI and resort was made to alcohol for crystallization. Needles mixed with well-defined granular crystals appeared. The granules (V) were separated (physic-

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ally) from the needles (VI) and, after two recrystallizations from alcohol, they melted at 102–103°. Anal. Calc. for $C_{11}H_{21}N_3S_4$: C, 40.83; H, 6.55; N, 12.98%. Found: C, 40.68; H, 6.61; N, 12.55%.

Conversion of V to VI

Compound V, 0.0605 gm., 2 ml. of alcohol, and one drop of aqueous acetic acid were refluxed for two minutes and the solvent evaporated. Recrystallization of the residue gave 0.054 gm. (98%) of colorless needles, m.p. 156–158° alone or mixed with VI.

Acetone and VI

A solution of 262 mgm. (0.883 mmole) of VI in 20 ml. of acetone was refluxed for 24 hr. It was cooled and the acetone evaporated under a stream of nitrogen. The residue was recrystallized from ethanol resulting in a 95% recovery of VI, m.p. 156–157°.

A similar experiment in which 15.4 mgm. (0.092 mmole) of dimethylammonium dimethyldithiocarbamate was included produced the same result. Obviously VI is not readily converted to II in excess acetone.

Tetramethylthiuramdisulphide (TMTD) and II

A solution of 240 mgm. (1.0 mmole) of TMTD and 177.3 mgm. (1.0 mmole) of II in 15 ml. of dry benzene was refluxed for 20 hr. On evaporation of the solvent, II was first recovered from the residue by leaching with warm water, producing needles, m.p. 56–58°. The final residue was then recrystallized from ethanol and 220 mgm. (92%) of TMTD, m.p. 156–157° alone or mixed with an authentic sample, was recovered.

Another run which included 3.8 mgm. (0.02 mmole) of dimethylammonium dimethyldithiocarbamate gave similar results. In neither case was there any evidence of the production of compound VI from II.

Attempted Synthesis of V

Compound VI, 381 mgm. (1.28 mmole), was dissolved in 500 ml. of absolute ethanol and treated with a large excess (25 ml.) of anhydrous dimethylamine. Anhydrous $MgSO_4$, 15 gm., was added and the suspension was placed on the shaker for 30 hr. at room temperature. After it was allowed to stand an additional $1\frac{1}{2}$ days, the drying agent was filtered off and the solvent and excess dimethylamine evaporated under dry nitrogen. The residue consisted of 360 mgm. of starting material, m.p. 156°. Refluxing with K_2CO_3 gave similar results.

Spectra

Absorption spectra of some of the products are given below.

The significant infrared absorption peaks[5] of chloroform solutions of II, IV,

[5]*The infrared data were obtained using a Perkin-Elmer No. 21 double beam recording spectrophotometer. The authors are indebted to Mr. R. W. White, Science Service Laboratory, for recording these data.*

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and VI are as follows, where S, M, and W indicate a strong, medium, and weak absorption:

II = $(CH_3)_2NCSCH_2CCH_3$

2920M, 1715S, 1495S, 1407W, 1380S, 1357S, 1277W, 1225*, 1150S, 1050W, 980S, 867W cm.$^{-1}$

IV = $(CH_3)_2NCSH \cdot HN(CH_3)_2$

2920S, 2670S, 2390M, 1485M, 1465S, 1410W, 1365S, 1245S, 1215*, 1120S, 1040W, 1025M, 967S, 890M, 660W cm.$^{-1}$

VI = $(CH_3)_2NCSCH_2CCH_2SCN(CH_3)_2$

2920M, 1717M, 1495S, 1407W, 1380S, 1290W, 1225*, 1147S, 1040M, 982S, 895M cm.$^{-1}$

A value marked with an asterisk is approximate, the exact peak being partially obscured by one due to chloroform.

The peak at 1357 cm.$^{-1}$ is due to the CH_3C—group and its presence in II and absence in VI confirms the symmetrical structure of VI.

In the near infrared[6] region of the spectrum freshly prepared acetone solutions of I, II, IV, VI, dimethylamine, and sodium dimethyldithiocarbamate exhibit no absorption. After two weeks at room temperature absorption peaks occur at 2620–2680, 2195, 2060, 1925, 1775, 1725, and 1435 millimicrons in all of the solutions. A similar absorption spectrum is obtained from acetone which has been refluxed with barium hydroxide, a procedure known to favor the production of diacetone alcohol.

In the ultraviolet region,[6] freshly prepared ethanol solutions of II, IV, and VI exhibit strong absorption with maxima at the following wavelengths:

IV: 289 and 254 millimicrons, both of which disappear when the solutions are left overnight at room temperature.

II and VI: 276, 246, and 216 millimicrons. These solutions appear to be stable.

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[6]*Ultraviolet and near-infrared data were obtained using a Beckman DK-1 recording spectrophotometer.*

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THE REACTION OF TETRAMETHYLTHIURAMDISULPHIDE WITH ACETONE

II. THE EFFECTS OF ADDITIVES[1]

By David Craig,[2] J. R. Robinson,[3] and Ray B. Fowler[2]

ABSTRACT

A discussion of the effects of additives upon the reaction of tetramethylthiuramdisulphide with acetone leads to the suggestion that the process is autocatalytic, that dimethylamine is the natural catalyst, and that the time required for its formation describes the induction period. The formation of the various products of the reaction is explained in terms of a free-radical mechanism.

The preceding paper (6) has cited the products which have been isolated from the reaction of tetramethylthiuramdisulphide (TMTD) with acetone. It was pointed out that the process exhibits an induction period, and it is the purpose of the present work to report on the effects of various additives upon this phenomenon and thence to draw certain conclusions regarding the probable course of the reaction.

Tetraethylthiuramdisulphide (Antabuse) is shown to be relatively stable towards acetone.

DISCUSSION

A. The Effects of Additives

All additives studied exerted their effect, if any, upon the rate of the reaction, the length of the induction period, and in one or two instances, the yields of the products. At no time did we observe a change in the chemical nature of the products. The reaction rates, product analyses, and a rough estimation of induction periods were studied using the macrotechniques described below. In order to extend the induction period and thus magnify its response to various additives, dilute solution studies were inaugurated and the reaction followed spectrophotometrically. The details of these are also to be found in the experimental part.

Among the additives which shorten the induction period are strongly basic primary and secondary amines and acetic acid. Relatively inactive or inert materials are weak nitrogen bases, water, sulphur, carbon disulphide, and tetramethylthiurammonosulphide. Inhibiting action was displayed by zinc oxide, acetic anhydride, and triethylamine. The latter seemed to shorten the induction period, but markedly slowed the reaction rate. Pyridine, a weak base, had little effect. Diphenylamine had no effect. Zinc oxide, in dilute solution, had no effect upon the induction period and yet this substance, which

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may be regarded as an insoluble base, effectively prevented the reaction in concentrated solution (Table I, expt. 17). It may be presumed, therefore, that the distance to the basic surface of the zinc oxide is simply too great, in dilute solution, for effective neutralization of the catalyst.

TABLE I

INDUCTION AND REACTION PERIODS AND MOLES OF REACTION PRODUCTS FOR THE REACTION OF 1.5 MOLES OF ACETONE, 0.1 MOLE OF TMTD, AND VARIOUS ADDITIVES

Expt. No.	Additive	Moles	Induction period, min.	Reaction period, min.	Products					II
					CS_2	IV	II	VI	V	VI+V
1	None	—	50	50	0.045	0.038	0.054	0.012	—	4.5
2[a]	None	—	175	45	.047	.049	.061	.013	—	4.7
3	Me_2NH	0.022	0	20	.047	.037	.059	.009	0.009	3.3
4[a]	Me_2NH	.0055	0	40	.036	.057	.074[d]	.008	—	9.3
5[a]	Et_3N[b]	.044	80	240	.034	.024	.043[d]	.024	—	1.8
6	Et_3N[c]	.022	50	145	.040	.036	.047	.021	—	2.2
7	C_5H_5N	.10	50	50	.053	.043	.058	.013	—	4.5
8[a]	Et_3N, Me_2NH	.044 .011	12	30	.037	.052	.045	.020	—	2.3
9[a]	Et_3N, IV	.004 .011	28	110	.034	.052	.052	.016	.007	2.3
10[a]	HOAc	.0067	15	40	.055	.050	.085	.004	—	21.0
11	CS_2[g]	.0053	83	48	.058	.040	.066[d]	.016	—	4.1
12	Sulphur	.12 gm.	87	45	.060	.044	.047[d]	.017	—	2.8
13[a]	TMTM[f]	.011	115	45	.053	.041	.071	.015	—	4.7
14[a]	II	.10	50	30	.053	.039	.041	.010	.005	2.7
15[a]	H_2O	.056	140	60	.053	.037	.073[d]	.013	—	5.6
16[a]	Me_2NH_2Cl	.011	50	60	.050	—	—	—	—	—
17	ZnO[e]	.20	>180	No reaction occurred						
18	Nitrogen stream	—	—	No reaction occurred						

[a]*Freshly crystallized TMTD, m.p. 161–162°, was used in this run. Material, m.p. 159–161°, was used in other runs.* [b]*Et_3N distilled from P_2O_5 but nevertheless contained 0.7% Et_2NH.* [c]*Et_3N contained 2% Et_2NH.* [d]*HOAc was used during isolation to convert enamines to ketones.* [e]*0.02 mole of TMTD was used and was recovered unchanged.* [f]*Tetramethylthiurammonosulphide.* [g]*The quantity of CS_2 added was not sufficient to interfere with the measurement of the induction period.*

Acetic anhydride, in the presence or absence of acetic acid, was an effective inhibitor. In the former case, about one per cent of tetramethylthiurammonosulphide was formed, revealing, presumably, the tendency of TMTD to dissociate into more stable substances. This monosulphide, when refluxed with acetone alone, was very slowly converted to tetramethylthiourea and carbon disulphide. It had a rather small effect, possibly due to trace impurities, on the induction period of the TMTD–acetone reaction but no effect on the rate. However, sulphur, an expected product along with tetramethylthiurammonosulphide from the decomposition of TMTD, sometimes shortened the induction period, sometimes lengthened it, as in experiment 12; the rate was unaffected. Table V shows how the inhibitory effect of acetic anhydride may be offset by the addition of an equivalent amount of dimethylammonium dimethyldithiocarbamate (IV).

The use of reagents such as acetic anhydride and zinc oxide to bind liberated dimethylamine chemically is presumably no more effective than purely phys-

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ical methods for removing this amine as fast as it is formed. Thus, there was little or no reaction in the concentrated solutions when acetone was allowed to escape slowly from the system, sweeping the amine out with it. An even more effective method was to pass a slow stream of nitrogen or air through the reflux above the system. This technique produced equally impressive results in the dilute solution studies (Table II).

TABLE II

EFFECT OF BASES ON THE INDUCTION PERIOD OF 12.5 MGM. (0.052 MM.) OF TMTD IN 20 ML. OF ACETONE

Base	(pK_H)[a]	mM. added	Induction period
Di-*n*-butylamine	(11.31)	0.01	240 min.
		0.06	60 "
		0.1	50 "
		0.2	30 "
Diethylamine	(10.98)	0.02	110 "
		0.04	50 "
		0.1	30 "
Dimethylamine	(10.71)	0.01	40 "
		0.02	25 "
		0.04	5–10 "
Dimethylammonium dimethyldithiocarbamate	(10.71)	0.004	50 "
		0.009	25 "
		0.02	5–10 "
Ammonia	(9.27)	0.06	90 "
		0.12	60 "
		0.36	25 "
		0.47	5–10 "
Pyridine	(5.26)	0.1	17 hr.
Triethylamine	(10.74)	0.006	15 "
		0.1	11.5 "
		0.2	8 "
Diphenylamine	(0.85)	0.1	20 "
Zinc oxide	— (Suspension)	0.001	20 "
Acetic acid	—	0.2	6 "
		0.4	6 "
		0.8	6 "
Reference solution	—	—	20 "
" " (under nitrogen stream)		—	>70 "

[a]pK_H *values: Hall, N. F. and Sprinkle, M. R. J. Am. Chem. Soc. 54: 3469. 1932.*

The dilute solution study also shows that dimethylammonium dimethyldithiocarbamate (IV) is a particularly effective activator of the reaction. It would appear that IV, at low concentration, is completely dissociated into dimethylamine and carbon disulphide, as in equation 4, p. 1606. It is equally evident that the effectiveness of the stronger nitrogen bases is proportional to their concentration.

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The data of Table III indicate the effect of TMTD concentration on the length of the induction period in the absence of additives. A few data are

TABLE III

EFFECT OF CONCENTRATION OF TMTD ON THE INDUCTION PERIOD IN 20 ML. ACETONE IN THE ABSENCE OF CATALYST

TMTD added, mM.	Induction period, hr.
0.052	20
0.10	15
0.25	12.5
0.50	10
1.0	5
2.0	3

presented in Table IV which compare the relatively stable *bis*-(diethylthiocarbamoyl)-disulphide (Antabuse) with TMTD, in the presence and absence of IV, in refluxing acetone.

TABLE IV

EFFECT OF DIMETHYLAMMONIUM DIMETHYLDITHIOCARBAMATE (IV) ON THE INDUCTION PERIOD OF 0.052 MM. OF TMTD OR ANTABUSE IN 20 ML. OF ACETONE

Weight of IV, mM.	Induction period	
	TMTD, min.	Antabuse, hr.
0	1200	150
0.004	50	25
0.01	25	20
0.02	5	3

TABLE V

EFFECT OF THE CONCENTRATION OF ACETIC ANHYDRIDE ON THE INDUCTION PERIOD OF 0.052 MM. OF TMTD IN 20 ML. OF ACETONE IN THE PRESENCE OR ABSENCE OF IV

Weight of Ac_2O added, mM.	Weight of IV added, mM.	Induction period, hr.
0	0	20
0.1	0	>150
0.01	0.01	1/3
0.03	0.01	>150

B. The Reaction Mechanism

von Braun has reported on the decomposition of TMTD (1) and it appears that any compound RH, where H is sufficiently labile, may be expected to react as shown in equation 1, p. 1606. This may be the initiating step in the TMTD–acetone reaction (equations 2 and 3). We have observed that the rate of this reaction is relatively slow when the TMTD is highly purified, although

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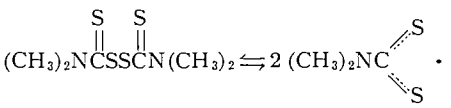
it varies with TMTD concentration (Table III). That dimethylamine is an effective promoter of the reaction is quite evident (Tables I, II, IV, V). Thus, in the absence of added amine, the reaction may be described as autocatalytic, and the induction period may be defined as the time required for the formation of the amine from TMTD. This conclusion is further supported by the observation that continuous removal of the amine, by chemical or physical means, results in an almost indefinite extension of the induction period (Tables I, II).

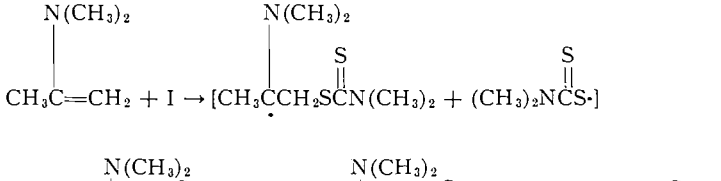
In order to explain the catalytic effect of dimethylamine, the presence of 1,3-*bis*-(dimethylthiocarbamoylthio)-2-dimethylamino-2-propene (V), as well as the absence of 1,1-*bis*-(dimethylthiocarbamoylthio)-2-propanone in the reaction residues, we are suggesting the course of reactions outlined by equations 5 to 9. The equilibrium described by equation 5 must be shifted far to the left, as earlier studies have shown (5) that, as a rule, aliphatic secondary amines and ketones do not readily form enamines in isolable amounts, even in the presence of dehydrating agents. Similarly, we were unable to prepare enamine V by treating the disubstituted acetone VI with dimethylamine.

If equation 5 is true, other amines with properties similar to those of dimethylamine (base strength, molecular size and shape, ability to form enamines, etc.) should also act as catalysts, and this is indeed the case (Table II). Within the strong-base group, there appears to be no correlation between pK_H values and observed effects. The pK_H values quoted, however, may have little significance for an acetone medium.

Equation 6 demonstrates the reaction of enamine VIII with further TMTD to form enamine VII,[4] thus regenerating dimethylamine through the unstable acid (III). Since TMTD is most likely to react as a resonance hybrid radical (4) it is convenient to assume a free-radical rather than an ionic mechanism:



The center of reactivity on the enamine VIII is likely to be similar to that of the corresponding enol (3) and the reaction with TMTD will be:[5]



VII IX III

[4]*The numbers assigned to the products are retained from Part I, and are not related to the sequence of the mechanism equations.*

[5]*The equations are not balanced; they are intended only to indicate the various radical species which may be present.*

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1. $(CH_3)_2NC(=S)SC(=S)N(CH_3)_2$ (I) $+ RH \rightarrow R{-}SC(=S)N(CH_3)_2 + (CH_3)_2NC(=S)SH$ (III)

2. I $+ CH_3C(=O)CH_3 \rightarrow (CH_3)_2NC(=S)SCH_2C(=O)CH_3$ (II) $+$ III

3. III $\rightarrow (CH_3)_2NH + CS_2$

4. $2(CH_3)_2NH + CS_2 \leftrightarrows (CH_3)_2NC(=S)SH.HN(CH_3)_2$ (IV)

5. $(CH_3)_2NH_2^+ + CH_3C(=O)CH_3 \leftrightarrows CH_3C(N(CH_3)_2)=CH_2$ (VIII) $+ H_2O$

6. VIII $+$ I $\rightarrow (CH_3)_2NC(=S)SCH_2C(N(CH_3)_2)=CH_2$ (VII) $+$ III

7. VII $+$ I $\rightarrow (CH_3)_2NC(=S)SCH_2C(N(CH_3)_2)=CHSC(=S)N(CH_3)_2$ (V) $+$ III

8. VII $+ H_2O \rightarrow (CH_3)_2NC(=S)SCH_2C(=O)CH_3$ (II) $+ (CH_3)_2NH$

9. V $+ H_2O \rightarrow (CH_3)_2NC(=S)SCH_2C(=O)CH_2SC(=S)N(CH_3)_2$ (VI) $+ (CH_3)_2NH$

10. 5 I $+ 4CH_3C(=O)CH_3 \rightarrow 3$ II $+ 2$ IV $+$ VI $+ 3CS_2 + (CH_3)_2NH$

Both VII and IX can react with water to give identical products:

VII *OR* IX $+ H_2O \rightarrow$ II $+ (CH_3)_2NH.$

It would appear, too, that both isomers could react with more TMTD:

VII $+$ I $\rightarrow$ V $+$ III

IX $+$ I $\rightarrow CH_2{=}C(N(CH_3)_2){-}CH(SC(=S)N(CH_3)_2)_2$ (X) $+$ III

and, on hydrolysis:

V $+ H_2O \rightarrow$ VI $+ (CH_3)_2NH$

X $+ H_2O \rightarrow CH_3C(=O)CH(SC(=S)N(CH_3)_2)_2$ (XI) $+ (CH_3)_2NH.$

However, since neither the unsymmetrical isomer XI nor any of its precursors was found in the residues, probably only VII reacts with TMTD. Presumably IX is completely removed by water or by rearrangement to VII.

Although neither of the enamines VII and VIII was isolated, their existence is postulated on the demonstrated presence of the higher molecular-weight (and apparently more stable) analogue (V). Also, it is only by assuming their formation that we can explain the facts reported in Part I, namely, that no 1,1-isomer of VI is found, that the monosubstituted acetone II is not an intermediate in the formation of the disubstituted VI, and that VI cannot be converted to II but is readily formed by the hydrolysis of V, as in equation 9. Furthermore, residues from which II and VI had been completely removed by crystallization were induced to produce much more of these materials by mild hydrolysis with dilute acetic acid. This clearly demonstrates the presence of both the intermediates V and VII.

As shown by equations 7, 8, and 9, products VI and II compete for the available enamine VII. Hence the ratio of these materials actually produced will vary largely with external influences, and the system is thus too complex to allow the writing of a simple stoichiometric equation. If we could assume complete conversion of IX to VII, an equal proportionation of VII, no loss of gaseous components, and equal rates for reactions 6 and 7, then the over-all process might be described by equation 10.

The action of triethylamine (Table I) lends further support to this mechanism. This base, somewhat like zinc oxide but less effective, stabilizes dimethylamine as the dithiocarbamate ion (2) and so lowers the reaction rate. It also depressed the production of II in favor of V+VI. By slowing down the over-all rate, the tertiary amine apparently allows reaction 7 to catch up with reaction 6, an effect which is markedly opposite to that of acetic acid. The shortening of the induction period by the tertiary amine is clearly a result of its contamination by a small amount of secondary amine; it cannot act catalytically because of its inability to form an enamine.

The catalyst effects of acetic acid are complex. In concentrated TMTD solutions it was a potent activator, but in dilute solution the effect was weak and independent of the acid concentration. Two opposing effects may be operative: (*a*) the suppression of the ionization of the acid III, thus leaving III available for dissociation into dimethylamine and carbon disulphide and (*b*) the formation of dimethylammonium ion. As dimethylammonium chloride was relatively inactive as a catalyst (Table I) it is assumed that the cation of this salt is inactive, and hence (*a*) appears to be the dominant effect in concentrated solution.

EXPERIMENTAL

The reaction of TMTD with acetone has an induction period which, for refluxing mixtures, can be estimated quickly by noting the time required to form carbon disulphide. Also, for mixtures in which the amount of TMTD exceeds its solubility (which is 0.028 mole of TMTD per 1.5 moles of refluxing acetone), the additional time required to effect complete solution gives an

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indication of the reaction rate. This is true, for example, of a mixture containing a ratio of 0.1 mole of TMTD to 1.5 moles of acetone, and Table I shows the effect of additives on the induction period, reaction time, and product composition resulting from such a mixture. If the operations were carried out in this way with a 100 ml. flask fitted with a stirrer and a vacuum jacketed $\frac{1}{4}$ in. $\times$ 24 in. nichrome wire coil column, it was possible to measure the time elapsing prior to CS_2 evolution. The column was fitted with a total reflux-variable take-off head. The low boiling point (38°) of the acetone–CS_2 azeotrope containing 67% CS_2 makes this method sensitive for detecting the formation of CS_2 in the refluxing mixture, i.e. the *end* of the induction period. The *reaction period* was considered to be the elapsed time between the appearance of CS_2 in the distillate and disappearance of solid TMTD in the refluxing mixture.

The residues from experiments such as these were first distilled to recover the excess acetone and CS_2; the latter was estimated by mixing the distillate with two volumes of water and weighing the lower layer. The distilland was then cooled to cause part of salt IV to crystallize. The liquor from this was then evaporated to dryness in a nitrogen stream and the residue crystallized from ether. The first fraction consisted of a mixture of IV and VI, subsequently separated by extraction with ether at room temperature. Compounds II and VI sometimes seem to crystallize with unexpected slowness apparently as a result of the existence in the reaction mixtures of the easily hydrolyzable enamines V and VII. Thus the sulphur runs (e.g., expt. 12, Table I) gave oily reaction mixtures from which II and VI were removed in the usual way. Much larger amounts of these compounds crystallized after the addition of 5 ml. of acetic acid to the alcoholic solution of the filtrates. VI forms a eutectic with about 98% of II, which melts at 56°.

Experiment 18 was repeated in two different ways. In one, acetone was allowed to evaporate through the reflux condenser so that 10 gm. was lost during eight hours. The reflux temperature, 55.0°, showed that no CS_2 was being formed. In a second, a stream of nitrogen was admitted to the reflux stream above the fractionating column at a rate just fast enough to evaporate 15 gm. of acetone to a dry-ice trap during 4.5 hr. Dimethylamine but no CS_2 was detected in the condensate. In this experiment an additional 10 gm. of acetone had been added to the charge. Again the reflux temperature remained at 55.0°. The reaction mixture was worked up to give a 96% recovery of TMTD.

Solubility of TMTD

The solubility of TMTD, m.p. 161–162°, in refluxing acetone was determined as follows. Six grams of TMTD was placed in a two-necked, 100 ml. flask which contained a glass-covered stirrer magnet. The flask was fitted with a small reflux condenser and with a small stoppered overflow for decanting liquid. A 21.8 gm. portion of acetone was added and the mixture refluxed 10 min. with stirring and the supernatant, which was clear, decanted to a tared crystallizing dish and quickly evaporated to dryness on a hot plate, under a nitrogen stream. The procedure was repeated with two additional 21.8 gm.

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portions and one 10.9 gm. portion of acetone. The extrahend remaining in the 100 ml. flask was quickly evaporated at reduced pressure to dryness between extractions. The weights and melting points of the extracts were respectively: 1.61 gm. (158–159°), 1.66 gm. (159–160°), 1.68 gm. (159–160°), and 0.85 gm. (158–159°). The final extrahend weighed 0.12 gm. and melted at 160–161°. Thus, 1.68 gm. of TMTD dissolves in 21.8 gm. of refluxing acetone. This corresponds to 6.70 gm. (0.028 mole) in 87.0 gm. (1.5 moles) of acetone, or approximately 61 gm. per liter of refluxing acetone.

Acetone and Tetramethylthiurammonosulphide

A solution of 6.4 gm. acetone (0.11 mole) and 20.8 gm. of the monosulphide in 60 ml. of benzene was refluxed for 40 hr. The mixture was then fractionated through a 0.25 in. × 16 in. coil column. The first fraction (4.36 gm.), b.p. 40–48°, based on its density, contained 3.5 gm. CS_2 and 0.86 gm. of acetone. The presence of carbon disulphide was confirmed by preparation of the piperidine derivative, m.p. in a sealed tube 170–172° alone or mixed with an authentic specimen. The next fractions were mainly benzene. The residue was crystallized from methanol to give 5.6 gm. of monosulphide, m.p. 107–109°. The filtrates were then evaporated in nitrogen and the residue extracted with water to give several fractions totalling 7.0 gm. and melting at 77–78°, alone or mixed with an authentic specimen of tetramethylthiourea.

Dilute Solution Studies

One batch of highly purified TMTD was used as a source for all the dilute solution studies and the experimental conditions were rigidly standardized so that the only variable in each run was the added catalyst. The reference solution consisted of 12.5 mgm. of TMTD (0.052 mM.) dissolved in 20 ml. of acetone, corresponding to about 2.9×10^{-4} mole of TMTD per 1.5 moles of acetone. A spectrum of the starting material (TMTD) was obtained at the beginning of each run and, as the solution was refluxed, samples were withdrawn at appropriate intervals and their spectra examined. It was found that the shape of the curve (optical density vs. wave length, see Fig. 1) would remain constant for a time and then, quite suddenly, would begin to change. The measured interval during which the spectrum remained constant was reproducible for a given mixture and was taken as the induction period. The data given in Tables II–V were obtained in this way. To ensure that the reaction had followed the expected course, each run was continued until the spectrum was formed and remained constant. The spectrum of each sample was recorded directly upon those preceding it; thus the earliest change in the shape of the curve was detected, and this was facilitated by scanning downward in wave length. Although not absolute values, the measured induction periods are comparable and they should reflect the relative effectiveness of the various additives as activators of the reaction.

In sampling, the reaction mixture was cooled and 50 lambdas (0.05 ml.) of solution was removed by micropipette. The acetone was completely removed from the sample at room temperature, *in vacuo*, and the residue was taken up in 3.5 ml. of absolute ethanol. With absolute ethanol in the reference cell, a

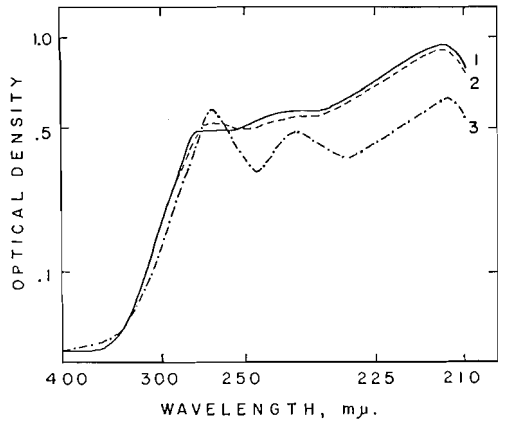

FIG. 1. The ultraviolet absorption spectra of: 1, TMTD at the beginning of the experiment; 2, the reaction products beginning to form at the end of the induction period; 3, the final products mixture.

Beckman recording spectrophotometer (Model DK-1) was used to obtain the spectrum in the ultraviolet region, 400–210 mμ. From the results shown in Table II it is seen that the reference solution has an induction period of 20 hr.

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INFRARED STUDIES OF SULPHUR-CONTAINING ORGANIC DERIVATIVES OF PHOSPHORUS PYROACIDS[1]

By R. A. McIvor, G. A. Grant, and C. E. Hubley

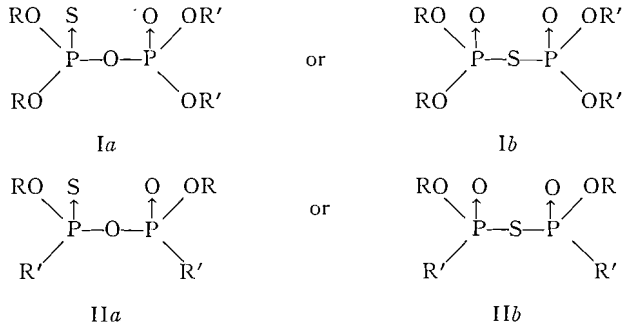
ABSTRACT

The assignments of several infrared bands of aliphatic phosphorus compounds have been reviewed and extended on the basis of new or improved data. These bands include POP, P → S, PSH, PSR, PH, and PCl. Several new assignments are proposed, mainly in the 12–24 μ region. Two examples are given of the application of these assignments to the determination of the structure of the thiopyrophosphates. It is shown that all procedures used for preparing monothiopyrophosphates yield exclusively the thiono isomer.

INTRODUCTION

In the course of studies on the chemistry of phosphorus pyroacids (6) extensive use was made of infrared spectra, both for determining the structure of the products and for assessing the purity of the intermediates. As the majority of the compounds were liquids, most of the spectra were determined as contact films. Although this method avoids solvent interference, no quantitative data on band intensities can be obtained directly.

The end products were I and II.



Ia Ib

IIa IIb

R′ and R = alkyl groups.

To determine which isomer was present, it was necessary to examine the spectra for the bands due to P → S, P—O—(P), P—S—(P), and RS, and to investigate the effects of environment on CH, P—O—(C), and C—O—(P) bands. From these studies it has been possible to make new assignments, some of which are well supported while others must be regarded as tentative.

EXPERIMENTAL

Preparation of most of the compounds examined is described elsewhere (6).

Unfortunately, it has not yet been possible to obtain all monothionopyrophosphates in a pure state. Chromatography has shown that the compounds

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corresponding to spectra Nos. 1, 7, and 8 are probably at least 90% one substance, and because of their interest, the spectra have been included. Bands due to known impurities have been marked.

A Baird double-beam recording spectrophotometer was used for all spectra. Band positions are cited to the nearest 0.01 μ for sharp bands and to the nearest 0.1 μ for broad bands when possible.

Toxic compounds were sandwiched between small windows (approximately $25 \times 10 \times 2$ mm.) and held in the microsample beam by a suitable holder. For decontamination the windows were dropped into alcoholic KOH. A macrocell was used for less toxic materials and decontamination was effected by washing the cell with a suitable solvent.

The two solid samples (spectra Nos. 25 and 36) were run as KBr pellets using a Hilger and Watts evacuable die. About 400 mgm. of KBr (ground to pass 200 mesh and dried in a vacuum oven at 50° C.) was mixed with 4 mgm. of sample in a hand mortar. The powder was then screened and pressed at 50° C. according to the die manufacturer's instructions.

Most spectra show overcompensation of atmospheric CO_2 absorption at 15 μ, an instrumental effect which always gives an inverted band and often distorts real bands in this region into false doublets.

RESULTS AND DISCUSSION

(*a*) P—O—P

Bergmann, Littauer, and Pinchas (2) assigned a band at 10.3–10.6 μ to P—O—P stretching, and report that it is not so apparent in the *n*-propyl and isopropyl esters. Corbridge and Lowe (3) note that this band shifts to longer wavelengths in polypyro compounds. It has been suggested in the above papers, and by Holmstedt and Larsson (5), that a band near 14.1 μ is associated with the P—O—P link. Mayhood and Harvey (7) have examined 14 compounds containing a P—O—P link and conclude that all absorb strongly in the 10.5–11.0 μ region, with the exception of tetramethyl pyrophosphate, which has a band at 10.3 μ (2) probably associated with the P—O—P link. They have also postulated* that when the P → O bond is replaced by P → S, the P—O—P band shifts to longer wavelengths and intensifies. They have been unable to assign any bands in the 14–15 μ region to the P—O—P linkage. Assignments are listed in Table I.

These data indicate that the 10.5–11.0 μ range suggested by Mayhood and Harvey should be extended downwards to 10.3 μ. This extension of the range discloses the possibility of confusing P—O—P compounds with those containing P—H and certain P—O—C groups (see below), so bands below 10.5 μ should be interpreted with caution. All the thiono compounds studied absorb at longer wavelengths than the corresponding oxygen compounds, and the P—O—P band is relatively more intense. In both the pyro and monothionopyro series the band shifts to longer wavelengths, as the alkyl group becomes larger, except in the ethyl compounds, which absorb at abnormally long wave-

* *Unpublished data.*

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TABLE I

ASSIGNMENTS FOR P—O—P, P → S, AND $-\overset{S}{\overset{\uparrow}{P}}-X$

Compounds	Ref.	Spectrum No.	Assignment in μ: P—O—P	P → S	$-\overset{S}{\overset{\uparrow}{P}}-X$
Tetramethyl pyrophosphate	2		10.31		
Tetramethyl monothionopyrophosphate		1	10.38	12.02	
Tetraethyl pyrophosphate	7	2	10.62		
Tetraethyl monothionopyrophosphate		3	10.64	12.02	
Tetraethyl dithionopyrophosphate		4	10.72	11.99	
Tetra-*n*-propyl pyrophosphate		5	10.42		
Tetra-*n*-propyl monothionopyrophosphate		6	10.5	11.6(m) (?) 12.9(?) (wk)†	
Tetraisopropyl monothionopyrophosphate		7	10.53		
Tetra-*n*-butyl pyrophosphate	4		10.50		
Tetra-*n*-butyl monothionopyrophosphate		8	10.58	12.25	
Di-isopropyl dimethylpyrophosphonate	7		10.58		
Di-isopropyl dimethylmonothionopyrophosphonate		9	10.68	12.50	
Di(isopropyl methylphosphonothionyl) methylphosphonothioate		10	10.83	12.46	
Phosphorothionic trichloride	4			13.35*	13.35*
Methylphosphonothionyl dichloride		11		12.69	14.95
Dimethyl hydrogen phosphonothioate		12		12.6	15.25, 15.7
Dimethyl phosphorodithioic acid		13		12.82(?)	15.2
Methyl phosphorodichloridothionate		14		12.06	13.8, 14.2
Dimethyl phosphorochloridothionate		15		11.98	15.05
Trimethyl phosphorothionate	4			12.1	
OOS-Trimethyl phosphorodithioate		16		12.22(?)	15.2
Diethyl hydrogen phosphonothioate		17		12.98(?)	15.2, 15.7
Diethyl phosphorodithioic acid		18		13.03(?)	15.25
Diethyl phosphorothioic acid		19		12.65	
Ethyl phosphorodichloridothionate		20		12.52	13.75, 14.3
Diethyl phosphorochloridothionate		21		12.25	15.2
Triethyl phosphorothionate		22		12.12	
OOS-Triethyl phosphorodithioate		23		12.08	15.2
Triethyl phosphorotetrathioate		24		14.55*	14.55*
SS-Di-(diethyl phosphorothionyl)-*O*-ethyl phosphorotrithioate		25		12.05	15.5
Di-*n*-propyl phosphorochloridothionate		26		11.63(?) 13.07(?)	15.05
Isopropyl methylphosphonochloridothionate		27		12.58	15.9
Di-isopropyl methylphosphonothionate		28		12.60	15.3
Di-isopropyl phosphorochloridothionate		29		12.67	
Di-*n*-butyl phosphorochloridothionate		30		12.35	15.05

**These compounds have only one band in this region.*
†In this table and subsequently; s, strong; m, medium; wk, weak; sh, shoulder; br, broad.

lengths. This abnormality, which is more marked in the pyro series than the monothionopyro series, is probably due to perturbation by the intense band near 10.3 μ found in all ethyl esters of phosphorus acids, but not in esters containing other alkyl groups. Although most of the compounds exhibited bands in the 13–15 μ region, we were unable to establish any useful correlations in this region with the P—O—P linkage.

(*b*) P → S

According to Bellamy (1), all previous results confirm the view that the P → S absorption occurs in the 13–17 μ region, with considerable variation in intensity, sometimes being completely undetectable. However, almost all of the compounds prepared here are observed to have P → S bands in the 12–13 μ region. Assignments are listed in Table I. With few exceptions, these compounds show a strong band in the 11.9–12.7 μ region, although where several ester groups are present the P → S band may possibly be weak but superimposed on strong ester bands. Even then, however, there is usually little difficulty in selecting the appropriate band.

When halogen, mercapto, or alkylthio groups are attached to P the P → S

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band shifts to slightly longer wavelengths, and a new, equally or more intense band appears in the 15 μ region (see below). The *n*-propyl esters examined showed no bands in this region, but two bands of medium or weak intensity near 11.6 μ and 13.0 μ. It is not definite which, if either, of these bands is associated with the P → S vibration, but the 13.0 μ band seems the more likely candidate (compare, for example, spectra 5 and 6). Two other exceptions to be noted are $PSCl_3$ and $PS(SEt)_3$, both of which exhibit only one band, at a position intermediate between the two bands normally expected in compounds of this type.

(*c*) —O—P—Cl, —O—P—S—, and R—P—Cl
(with S below each P)

Monochloro and monothiolo phosphorothionates exhibit a strong band near 15 μ. This band is shifted towards 14 μ, frequently with doublet formation in dichloro compounds. The corresponding phosphonochloridates and dichloridates absorb near 16 μ and 13 μ, respectively. In addition P(S)H compounds contain a weak doublet in this region which may arise, however, from the P—S—(H) stretching in the trivalent tautomer. $PSCl_3$ and $PS(SEt)_3$ are somewhat anomalous (see above). The wavelengths of maximum absorption for this band are given in Table I.

That this band should be due to P → S vibration seems improbable in view of the fact that in other than chloro compounds, the P → S seems to be nearer 12 μ, and in series of the type $ROPSCl_2$, $(RO)_2PSCl$, $(RO)_3PS$, a band is observed in the 12–12.6 μ region, which shifts gradually to shorter wavelengths. In compounds of the type —O—P—S—C the band might be attributed to the
(with S below P)
C—S—(P) bond. This assignment also seems unlikely since compounds of the type —P—SH and —P—S—P—, which contain no C—S bonds, have a
(with S below each P)
similar band. We are unable to attribute this band to any particular vibration, but because of its intensity and location, it has proved exceedingly useful for identifying compounds or for assessing their purity.

(*d*) C—H *Deformation*

It was noted in this work that the shape of the CH deformation bands depends both on the nature of the alkyl group and the nature of the substitution, which observation can be very useful in determining the structure of a compound. It is well established (1) that CH_2 gives a band near 6.85 μ while CH_3 has an asymmetrical deformation at 6.9 and a symmetrical one at 7.27 and CH gives a weak band near 7.46 μ. Our assignments are as follows:

(1) MeO *bands.*—In phosphorus esters containing a methoxyl group, a single band appears at about 6.85 μ, which varies only slightly between MeO—P(O) and MeO—P(S). Small differences in shoulders of this band are noticed from compound to compound. P—Me groups do not have this band

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but give rise to another band near 7.15 μ in both MeP(O) and MeP(S) compounds. Dimethyl methylphosphonate has both bands. In addition there is the well-known P(O)—Me absorption near 7.6 μ, which is shifted to 7.7 μ in P(S)—Me compounds.

(2) EtO *bands.*—Compounds containing an Et—O—P(O) link exhibit four characteristic bands, near 6.75, 6.92, 7.17, and 7.3 μ, usually increasing in intensity in that order. In compounds of trivalent phosphorus as well as in EtO—P(S) and EtO—P(O)—SR compounds, the 7.3 μ band disappears. EtS—P bands and Et—P bands are superimposed on these bands when present. EtS—P compounds containing no EtO absorb at 6.9, 7.05 (sh), 7.28, and 7.9 while Et—P compounds absorb at 6.85 and 7.15 μ.

(3) *n*-PrO *bands.*—On the basis of a few examples, the following tentative assignments have been made:
PrO—P(O): 6.77(sh), 6.82(s), 6.93(sh or wk), 7.18(m), 7.24(wk or sh), 7.4(v.wk). PrO—P(S): 6.82(s), 6.93(sh or wk), 7.18(m), 7.24(small sh). It is thus seen that the 6.77 shoulder and 7.4(v.wk) bands have disappeared in the P(S) compounds, and the 7.24 shoulder has diminished in intensity. No compounds containing P—Pr or P—S—Pr bands have been investigated.

(4) *i*-PrO *bands.*—Compounds containing *i*-PrO—P(O) bonds have bands at 6.78(sh), 6.81(m), 6.88(sh), 7.2 and 7.26 (strong doublet with 7.2 band slightly more intense), 7.39 μ (v.wk). In *i*-PrO—P(S) compounds the 6.78 shoulder disappears, the 6.88 shoulder becomes a band, the 7.26 μ band becomes considerably more intense than the 7.2 μ, and the 7.39 μ band is absent. The positions are almost identical for *n*-PrO and *i*-PrO bands, but the relative intensities differ. In *n*-PrO compounds the 6.8 μ band is about double the intensity of the 7.2 μ band whereas in *i*-PrO compounds the reverse is true.

(5) *n*-Bu *bands.*—The CH deformation bands for BuO—P(O) and BuO—P(S) compounds differ little, and are qualitatively the same as for PrO groups. BuO—P compounds give rise to bands at 6.77(sh), 6.82(s), 6.98(wk or sh), 7.2(wk.sh), 7.24(m). Substitution of P(S) for P(O) weakens the 6.77 μ shoulder, strengthens the 6.98 μ band, and weakens the 7.2 μ shoulder. BuO compounds differ from *n*-PrO compounds in a reversal of intensity of the 7.2 μ and 7.24 μ bands.

(6) *Cyclohexyloxy bands.*—$C_6H_{11}OP(O)$ compounds exhibit two very sharp bands at 6.88 μ and 7.28 μ with a small shoulder at 6.82 μ. No compounds containing $C_6H_{11}OP(S)$ have yet been investigated.

(*e*) *The* C—O—(P) *and* P—O—(C) *Vibrations*

As these bands are usually very intense they have been fairly extensively investigated (1, 4, 7). The usual assignments for C—O—(P) are in the 8.4–9.0 μ region and for P—O—(C) from 9.5 to 10.5 μ. The former are sharp and of medium intensity, while the latter usually give rise to a broad, very strong, complex absorption between 9.5 and 10.5 μ. Other bands, due to P—H, P—OH, P—SH, C—C, C—C—O, and C—N, may also fall in this region, increasing the complexity of the band. It is worth while, however, to discuss these bands

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individually, emphasizing the effects of various alkyl groups and environment of the phosphorus atom.

(1) MeO *compounds*.—Compounds containing a MeOP linkage show a sharp band of medium intensity near 8.4 μ and a very strong broad band between 9.5 and 9.85 μ. In MeOP(O) compounds, the lower band is found between 8.4 and 8.43 μ, and the longer wavelength band near 9.5 μ. In MeOP(S) compounds, the corresponding bands are near 8.45 μ and 9.7 μ, while in trivalent MeOP compounds the latter band is near 9.85 μ.

(2) EtO *compounds*.—Compounds with ethoxy groups attached to phosphorus exhibit a sharp band of medium intensity from 8.56 to 8.60 μ, in EtOP(O) compounds, and from 8.58 to 8.62 μ in EtOP(S) and trivalent compounds. As the number of ethoxyl groups increases from one to three this band shifts slightly to shorter wavelengths. A weak band occurs between 9.03 and 9.1 μ, usually at 9.05 μ, in all types of EtO—P compounds. The next band at longer wavelengths in all EtO—P compounds is between 9.65 and 9.72 μ for EtO—P(O) and trivalent compounds, and between 9.7 and 9.9 μ for EtO—P(S) compounds. This band also shows a slight shift to shorter wavelengths as the number of ethoxy groups increases. Another band appears between 10.1 and 10.6 μ whose intensity varies markedly with the number of ethoxy groups, and which shifts toward longer wavelengths as the number of ethoxy groups increases, or when P—R or P—S—R groups are present. EtO—P(O) compounds absorb in the 10.1–10.3 μ region, EtO—P(S) compounds from 10.2 to 10.6 μ, and trivalent EtO—P compounds near 10.9 μ.

(3) *n*-PrO *compounds*.—A weak band is found in these compounds near 8.65 μ, as well as shoulders near 9.1 μ and from 9.4–9.5 μ regardless of the environment of the phosphorus atom. The P—O—(C) absorption is between 9.80 and 9.85 μ in PrO—P(O) compounds and at 9.98 μ in the one PrO—P(S) compound examined.

(4) *i*-PrO *compounds*.—Isopropoxy compounds have three very characteristic sharp bands of medium intensity at 8.45 μ, 8.7 to 8.72 μ, and 8.98 to 9.02 μ. The P—O—(C) band occurs between 9.88 and 10.1 μ in all cases. In addition, most compounds containing a P—C link have an additional band in the 10.15–10.25 μ region.

(5) *n*-BuO *compounds*.—These compounds have two very weak bands at 8.68 and 8.9 μ, a shoulder or band between 9.3 and 9.4 μ, and a very strong, broad band between 9.65 and 9.8 μ (usually about 9.7 μ). P—C compounds have an additional band at 10.2 μ and tributyl phosphite one at 10.4 μ.

(6) *Cyclohexyloxy compounds*.—The few compounds examined have weak bands at 8.62 and 8.85 μ, a band or shoulder at 9.6 μ, a strong band at 9.8 μ, and tricyclohexylphosphite has an additional strong band at 10.25 μ.

In summary, the C—O—(P) band is most characteristic of the alkyl group, although the P—O—(C) does show environmental changes for the lower molecular weight groups. Trivalent compounds either show a bathochromic shift of the P—O—(C) band or have a new band at longer wavelengths.

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(f) The P—H *Vibration*

Only the P—H stretching vibration near 4.1 μ has yet been assigned (1). However, it is noted that all compounds examined containing a P(O)H link (see Table II) also absorb near 9.2, 10.2, and 18.0 μ, although most alkyl

TABLE II

P—H ASSIGNMENTS

Compounds	Ref.	Spectrum No.	Assignment in μ			
Dimethyl hydrogen phosphonate	8	31K	4.13	10.21	18.3	20.0
Diethyl hydrogen phosphonate	8	32K	4.13	10.3	18.2	19.5
Di-isopropyl hydrogen phosphonate	8	33K	4.13	10.22	18.1	18.9(sh)
Di-*n*-propyl hydrogen phosphonate		35,35K	4.13	10.22	18.2	18.9(br.sh)
Di-*n*-butyl hydrogen phosphonate	4	34K	4.13	10.22	18.1	18.9(sh)
Dimethyl hydrogen phosphonothionate		12,12K	4.18	10.5	21.1	
Diethyl hydrogen phosphonothionate		17,17K	4.18	10.6	20.6	

alkylphosphonates and many other compounds (1) also absorb near 10.2 μ, and the 9.2 band is often submerged in the P—O—(C) absorption. P(S)H compounds have the corresponding bands at 4.2, 9.2, 10.5 to 10.6, and 21 μ, as well as the doublet mentioned in section (*c*).

(*g*) *The* P—C (*Alkyl*) *Stretching Vibration*

Bellamy (1) reports that this vibration is weak, and that as it may lie in the 12–13 μ region it is doubtful whether useful correlations could be obtained. However, we have noted bands, probably connected with the P—C vibration in Me—P and Et—P compounds, which are fairly constant and which may be useful for verifying the presence of such a group. In addition to the 11 to 15 μ bands Et—P also shows an 8.15 μ band, probably corresponding to the 7.6 μ Me—P band, and most P—C compounds also have weak, broad bands in the 18–20 μ region near those assigned to P—Cl linkages (Table III).

TABLE III

P—C ASSIGNMENTS

Compounds	Ref.	Spectrum No.	Assignments in μ		
Methylphosphonyl dichloride		36		11.2	
Methylphosphonothionyl dichloride		11	11.0(s)		11.2(sh)
Dimethyl methylphosphonate	8			10.97	
Diethyl methylphosphonate	8		10.9(?)		11.1
Isopropyl methylphosphonochloridothionate		27	10.9(?)		11.15
Di-isopropyl methylphosphonate	8		10.9(?)		11.1
Di-isopropyl methylphosphonothioate		28	11.0		
Di-isopropyl dimethylmonothionopyrophosphonate		9	11.25		
Di(isopropyl methylphosphonothionyl) methylphosphonothionate		10	11.55		
Cyclohexyl methylphosphonochloridate		49	10.8(?)		11.2
Sodium cyclohexyl methylphosphonate		50		11.2	
Dibutyl methylphosphonate		37		10.85	
Ethylphosphonyl dichloride		38	8.15	13.25	13.85
Diethyl ethylphosphonate	8		8.15	13.4	14.3
Di-isopropyl ethylphosphonate	8		8.15	13.4	14.2
Di-*n*-butyl ethylphosphonate		39	8.15	13.4	14.4

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(*h*) P—S—(C) *and* C—S—(P) *Stretching Vibrations*

Information available suggests that C—S—(P) gives rise to a weak band between 15.5 and 16 μ while P—S—(C) gives rise to bands near 16.5 and 17.5 μ for (O)—P—S—(C) compounds and near 18.6 and 19.4 μ for (S)P—S—(C) compounds. An additional tentative assignment of 17.7(s) μ and 19.0(sh) μ is made for trivalent P—S—(C) compounds (Table IV).

TABLE IV

P—S—(C) AND C—S—(P) ASSIGNMENTS

Compounds	Spectrum No.	Assignments in μ		
Triethyl phosphorotrithioite	*	15.7	17.7	19.0(sh)
OOS-Trimethyl phosphorothioate	*	16.5		17.6
OOS-Triethyl phosphorothioate	40,40K	15.5	16.5	17.5
SSS-Triethyl phosphorotrithioate	41,41K	15.7		17.9
OOS-Trimethyl phosphorodithioate	16K	18.8		19.7
OOS-Triethyl phosphorodithioate	23K	18.6		19.2
Triethyl phosphorotetrathioate	24K	15.6		19.1

**Although there is no doubt about the position of these bands, the compounds were not obtained sufficiently pure to warrant including their spectra.*

The 15.6 μ band is in addition to the very strong band described in section (*c*) associated with the P(S)—S— linkage and is attributed to C—S—(P) since it varies little with the substitution on the phosphorus atom. The triesters have only one very intense band beyond 16 μ, whereas the mono- and di-esters have two, the one at shorter wavelengths being the weaker. These bands are attributed to the P—S—(C) link.

(*i*) P—S—(H) *Stretching Vibrations*

Little has been reported in the literature concerning the position of absorption due to this vibration. Our results tend to indicate that this absorption is close to that due to P—S—(C) but at slightly longer wavelengths. When P(S) groups replace P(O) groups the band shifts to longer wavelengths (Table V).

It will be noted that the band positions in the spectrum of the ion differ little from those of the acid in the one case studied, but the bands are sharper and the relative intensities are reversed.

TABLE V

P—S—(H) ASSIGNMENTS

Compounds	Spectrum No.	Assignments in μ	
Dimethyl phosphorodithioic acid	13K	19.0	20.3
Diethyl phosphorothioic acid	19K	15.4	16.2
Diethyl phosphorothioic acid, triethylamine salt	42K	15.4	16.3
Diethyl phosphorodithioic acid	18K	18.5	19.7

(*j*) P—S—(P) *Stretching Vibrations*

By analogy with the behavior of P—O—(C) and P—O—(P) bands, the P—S—(P) would be expected to absorb at somewhat longer wavelengths than

the corresponding P—S—(C) bands. None of the esters of phosphorus monothiopyroacids prepared in this work show any bands in the 12–26 μ region, except a few containing P—S—(C) impurities. However, one compound containing P(S)—S—P(S) has been prepared and examined. Attempts to synthesize other compounds containing P(S)—S—P(S) and P(O)—S—P(S) seem to have been partially successful, but all attempts to obtain them in a pure state have resulted in the decomposition of the small amount present. *SS*-Di-(diethyl phosphorothionyl)-*O*-ethyl phosphorotrithioate (spectrum No. 25K) has bands at 20.0 μ and 21.7 μ, while an impure sample of what was probably *OOOO*-tetraethyl trithiopyrophosphate had a band at 20.5 μ not present in the starting materials.

(*k*) *The* P—Cl *Stretching Vibration*

Daasch and Smith (4) have reported that P—Cl bands occur from 19 to 23 μ, usually giving a doublet when two or more chlorines are present and a single band when one chlorine is present. Our results are summarized in Table VI.

TABLE VI

P—Cl ASSIGNMENTS

Compounds	Ref.	Spectrum No.	Assignment in μ			
(i) Trivalent P						
Phosphorus trichloride	4		19.6			20.5
Phenyl dichlorophosphine	4				20	
Ethyl dichlorophosphine	4		19.9			20.5
(ii) O ↑ P—Cl						
Phosphorus oxychloride	4		17.2			20.6
Methylphosphonyl dichloride		36K	18.3			20.2
Ethylphosphonyl dichloride		38K	17.6		18.5	20.0
Dimethyl phosphorochloridate		43K	16.7			18.1
Diethyl phosphorochloridate		44K	16.7			18.1
Di-*n*-propyl phosphorochloridate		45K	16.7			18.0
Di-isopropyl phosphorochloridate		46K	16.7			18.0
(iii) S ↑ P—Cl						
Phosphorothionyl trichloride	4		18.6			23.1
Methylphosphonothionyl dichloride		11K	19.4			22.2
Methyl phosphorodichloridothionate		14K	18(?)	18.8	21	22.1
Ethyl phosphorodichloridothionate		20K	18.1(?)	18.9(?)	20.5	21.3
Dimethyl phosphorochloridothionate		15K		19.0		20.5
Diethyl phosphorochloridothionate		21K		18.7		20.1
Di-*n*-propyl phosphorochloridothionate		26K		18.5		19.7
Di-isopropyl phosphorochloridothionate		29K		18.5		19.7
Di-*n*-butyl phosphorochloridothionate		30K		18.5(sh)		19.3

Although there is considerable variation in each group depending on the number of halogen substituents and whether P—C links are present, P(O)Cl compounds usually absorb in the 17–18 μ region, P(S)Cl compounds in the 18–20 μ region, and trivalent phosphorus compounds close to 20 μ.

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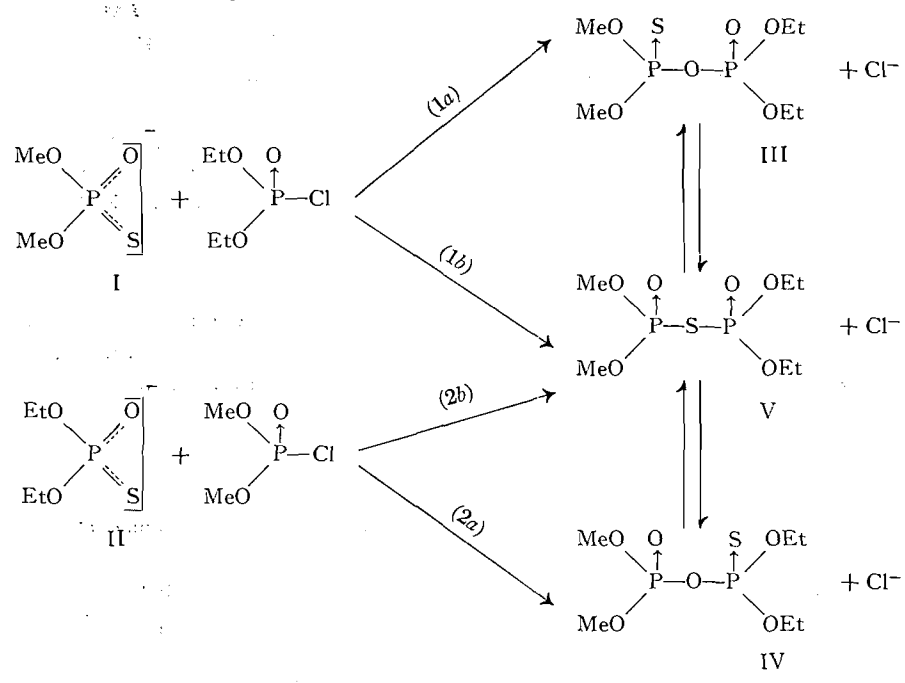
Application

To establish the usefulness of these correlations, reactions (1) and (2) were carried out and the products examined.



When ions I and II are treated with alkyl halides, reaction takes place almost exclusively at the sulphur atom. If this occurred when dialkyl phosphorochloridates were used, both reactions would yield the same P—S—P isomer V. Since previous experience has shown that the final product of this type of reaction is a thiono isomer, V if formed would be expected to rearrange to III, IV, or a mixture of the two. In either case the same product or mixture should result. If, however, reaction took place only at the oxygen atom, reaction (1) should give only III, and reaction (2) only IV, unless interconversion of III and IV via V if possible. Infrared absorption would be the only physical property which would readily distinguish between these possibilities.

On the basis of the correlations given earlier, some of the features expected in the spectra of III and IV were predicted. Both compounds would be expected to have a P → S band near 12 μ and a P—O—P band near 10.5 μ. The main differences were expected in the CH and alkyl group deformation.

Structure III would be expected to have a MeO band near 6.85 μ, superimposed on the EtO—P(O) bands at 6.75, 6.92, 7.17, and 7.3 μ, while structure IV would lack the 7.3 μ band. The sharp characteristic C—O—(P) bands of MeO and EtO should both be present, at approximately 8.45 μ and 8.58 μ for structure III, and 8.41 and 8.60 μ for structure IV, qualitatively a greater separation for IV. Owing to the breadth and intensity of the P—O—(C) bands, differences would be less noticeable, but III should exhibit intense absorption in the 9.65 μ to 9.8 μ region and have a second band near 10.2 μ, while IV

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TABLE VII

OBSERVED BANDS

	III (Diethyl phosphoryl) dimethyl phosphorothionate	IV Diethyl (dimethyl phosphoryl) phosphorothionate
P → S	12.05	12.05
P—O—P	10.5	10.5*
CH	6.75, 6.85, 6.9, 7.17, 7.3	6.78, 6.85, 6.92, 7.2
C—O—(P)	8.45, 8.55	8.42, 8.59
P—O—(C)	9.62, 10.25	9.4–9.8, 10.4*

**P—O—(C) and P—O—(P) not resolved.*

INDEX TO SPECTRA

	Spectrum No.
Cyclohexyl methylphosphonochloridate	49
Di-*n*-butyl ethylphosphonate	39
Di-*n*-butyl hydrogen phosphonate	34
Di-*n*-butyl methylphosphonate	37
Di-*n*-butyl phosphorochloridothionate	30
SS-Di(diethyl phosphorothionyl)-*O*-ethyl phosphorotrithioate	25
Diethyl (dimethyl phosphoryl) phosphorothionate	48
Diethyl hydrogen phosphonate	32
Diethyl hydrogen phosphonothionate	17
Diethyl phosphorochloridate	44
Diethyl phosphorochloridothionate	21
Diethyl phosphorodithioic acid	18
Diethyl phosphorothioic acid	19
Diethyl phosphorothioic acid, triethylamine salt	42
(Diethyl phosphoryl) dimethyl phosphorothionate	47
Di-isopropyl dimethylmonothionopyrophosphonate	9
Di-isopropyl hydrogen phosphonate	33
Di-isopropyl methylphosphonothionate	28
Di(isopropyl methylphosphonothionyl) methylphosphonothionate	10
Di-isopropyl phosphorochloridate	46
Di-isopropyl phosphorochloridothionate	29
Dimethyl hydrogen phosphonate	31
Dimethyl hydrogen phosphonothionate	12
Dimethyl phosphorochloridate	43
Dimethyl phosphorochloridothionate	15
Dimethyl phosphorodithioic acid	13
Di-*n*-propyl hydrogen phosphonate	35
Di-*n*-propyl phosphorochloridate	45
Di-*n*-propyl phosphorochloridothionate	26
Ethylphosphonyl dichloride	38
Ethyl phosphorodichloridothionate	20
Isopropyl methylphosphonochloridothionate	27
Methylphosphonothionyl dichloride	11
Methylphosphonyl dichloride	36
Methyl phosphorodichloridothionate	14
Sodium cyclohexyl methylphosphonate	50
Tetra-*n*-butyl monothionopyrophosphate	8
Tetraethyl dithionopyrophosphate	4
Tetraethyl monothionopyrophosphate	3
Tetraethyl pyrophosphate	2
Tetraisopropyl monothionopyrophosphate	7
Tetramethyl monothionopyrophosphate	1
Tetra-*n*-propyl monothionopyrophosphate	6
Tetra-*n*-propyl pyrophosphate	5
OOS-Triethyl phosphorodithioate	23
Triethyl phosphorotetrathioate	24
OOS-Triethyl phosphorothioate	40
Triethyl phosphorothionate	22
SSS-Triethyl phosphorotrithioate	41
OOS-Trimethyl phosphorodithioate	16

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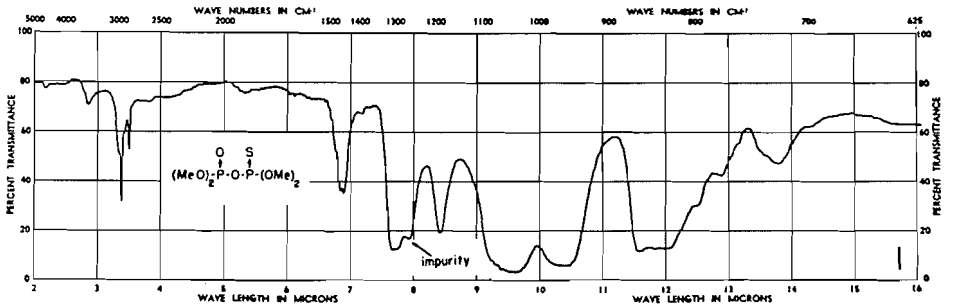

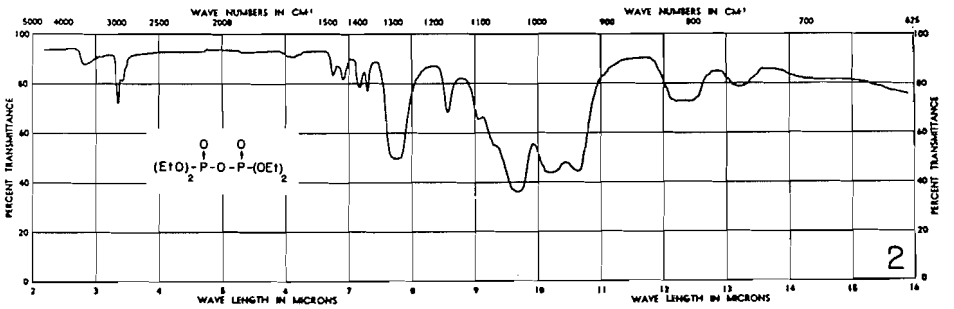

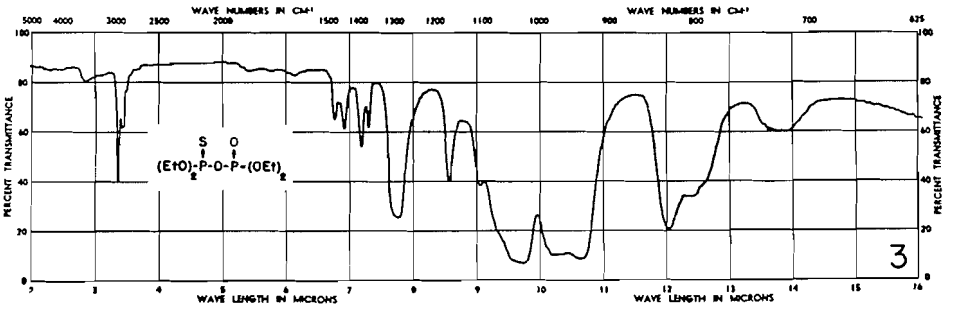

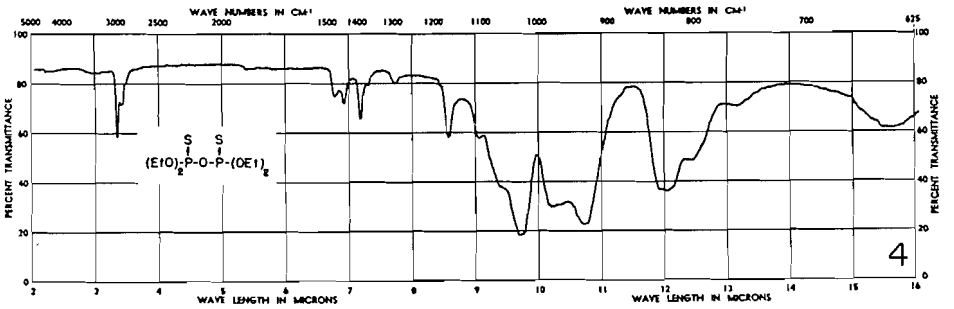

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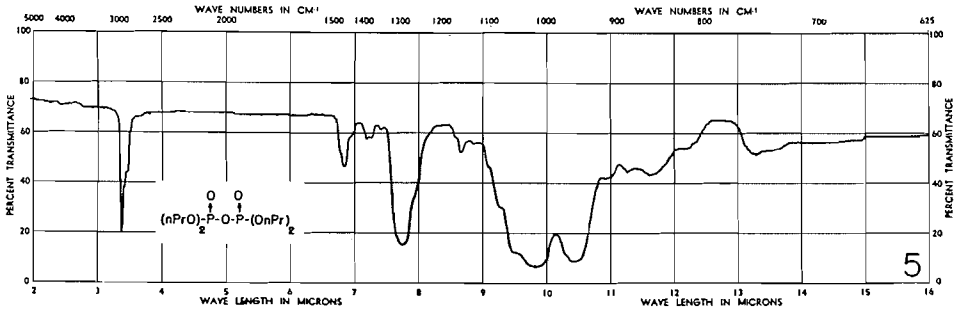

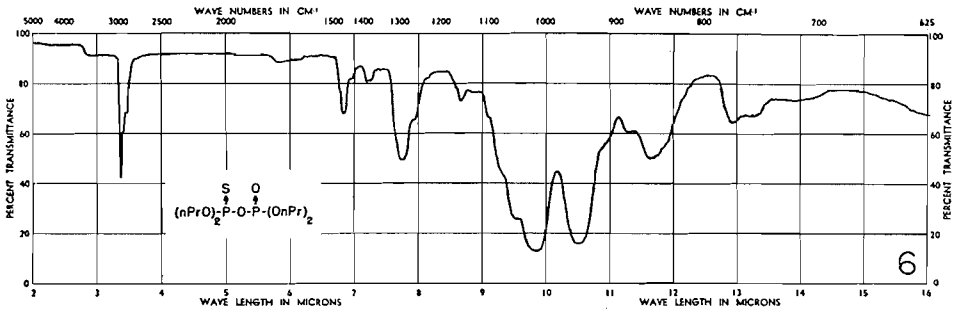

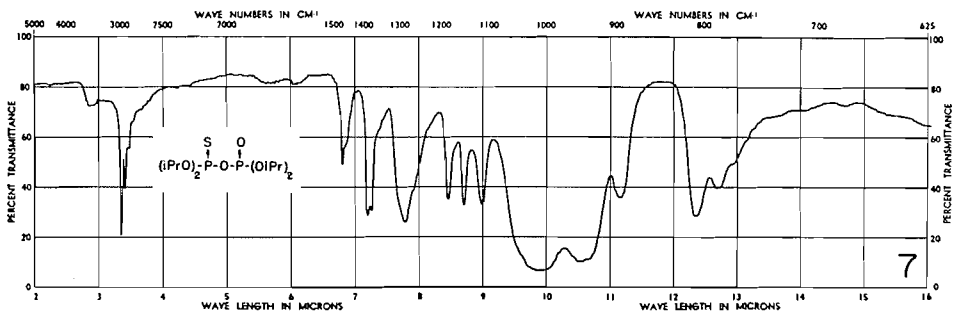

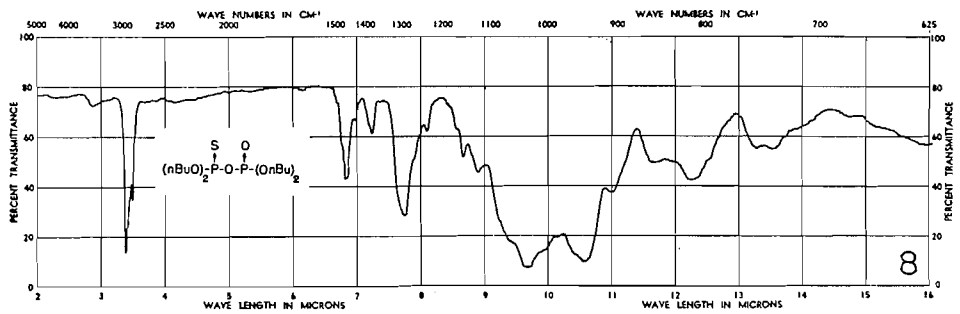

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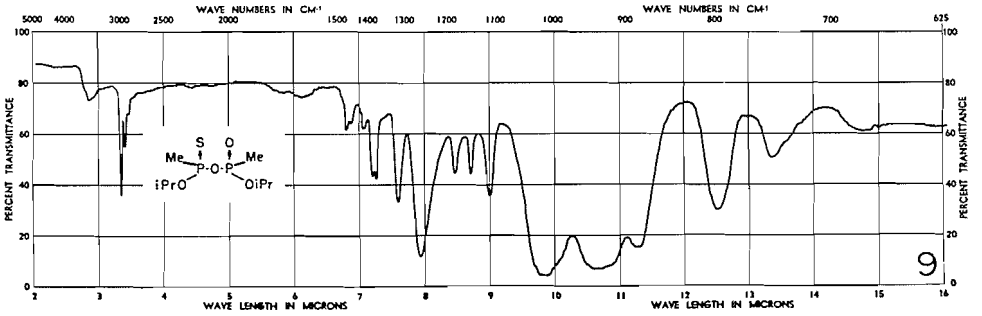

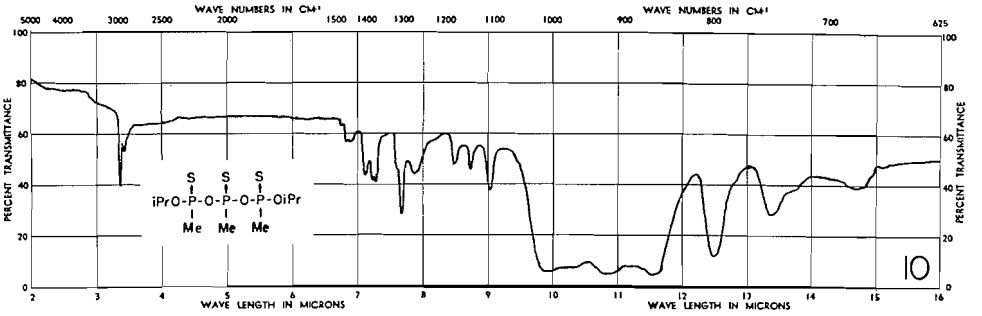

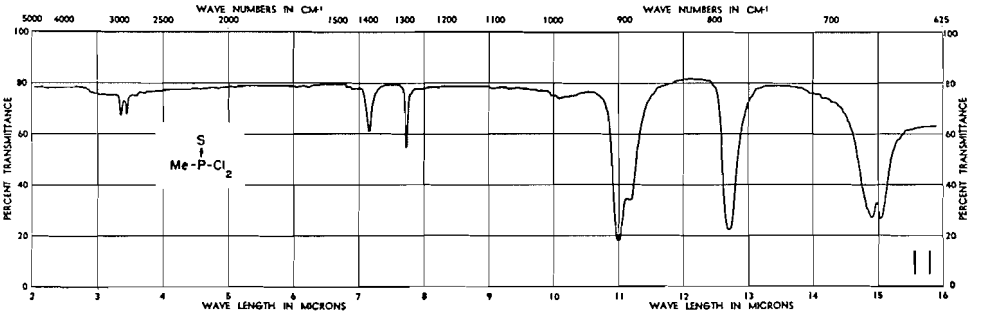

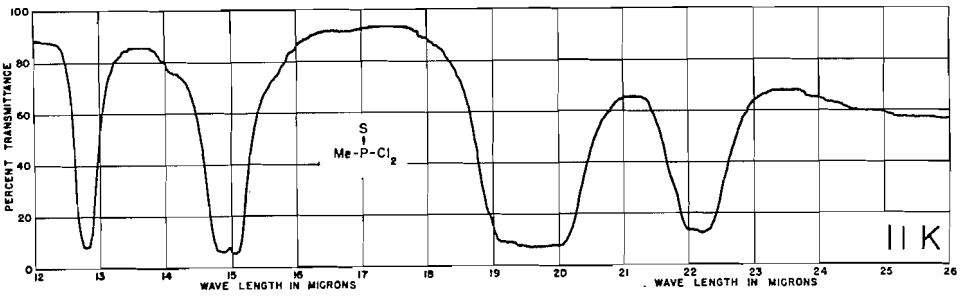

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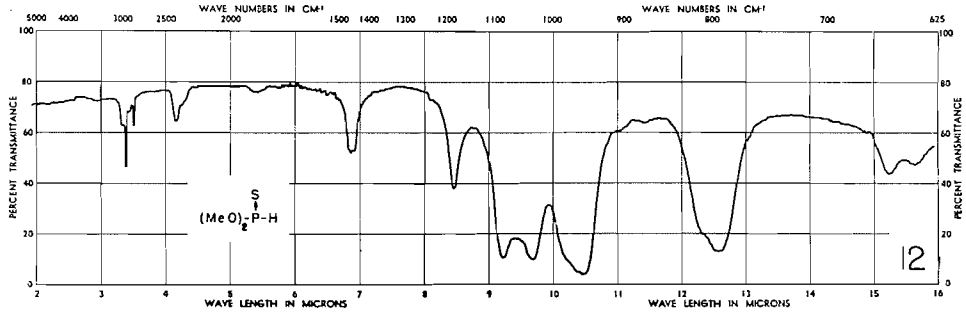

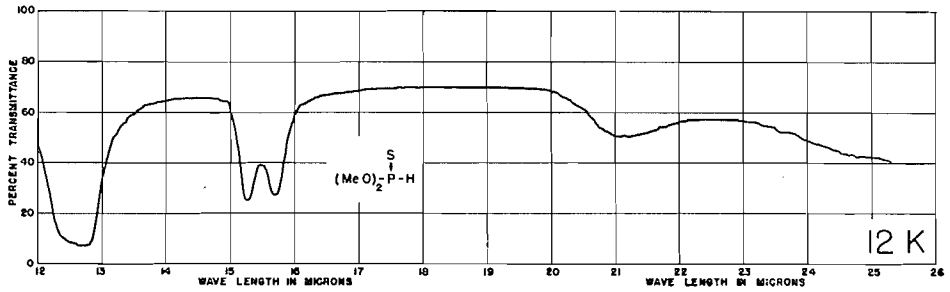

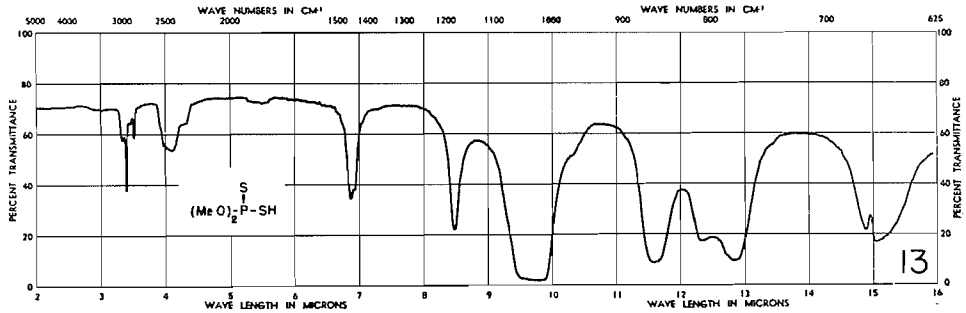

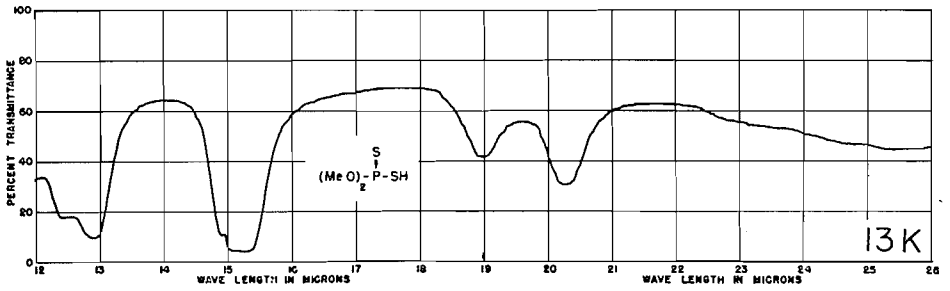

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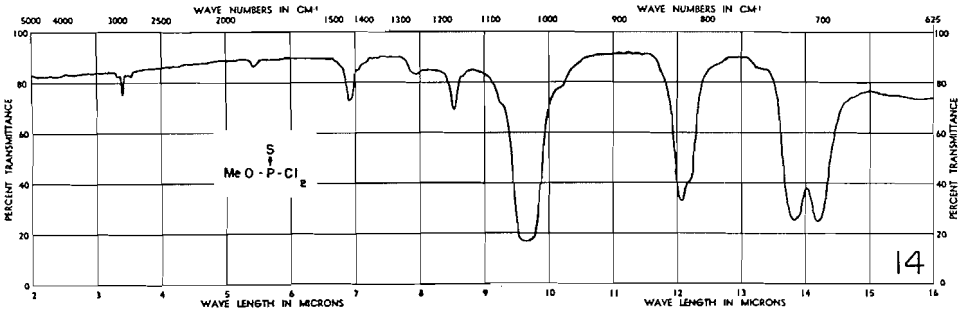

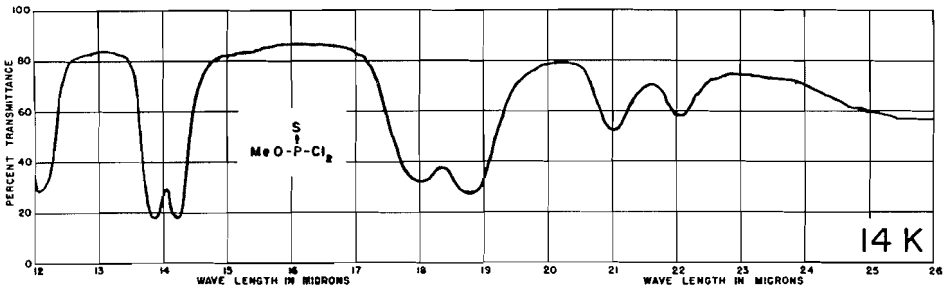

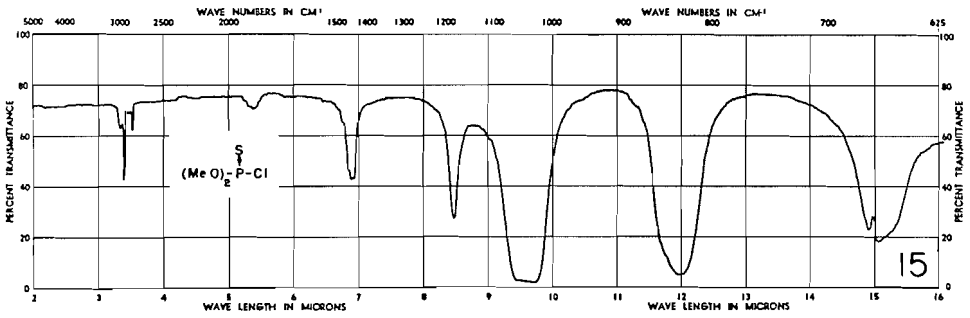

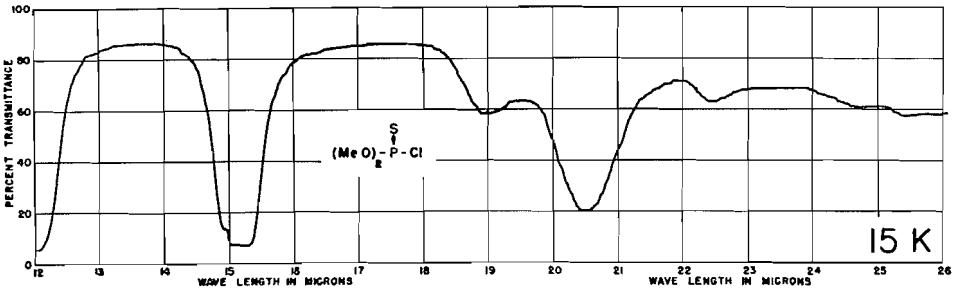

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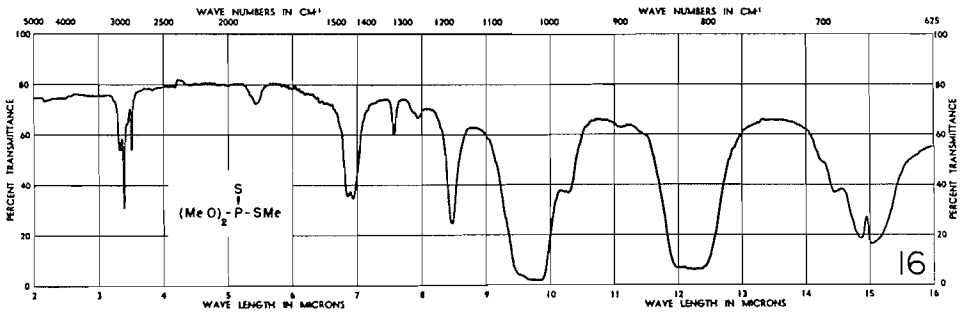

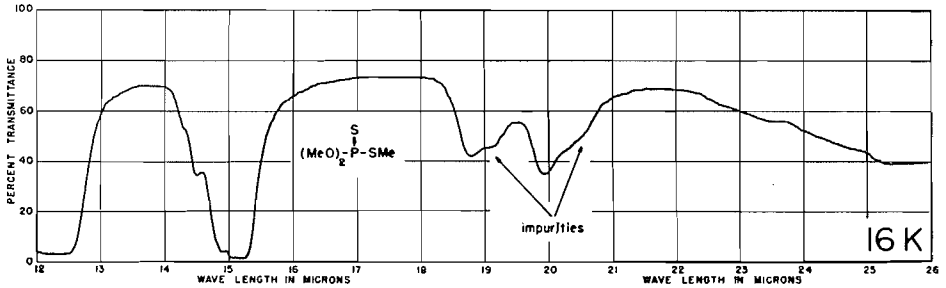

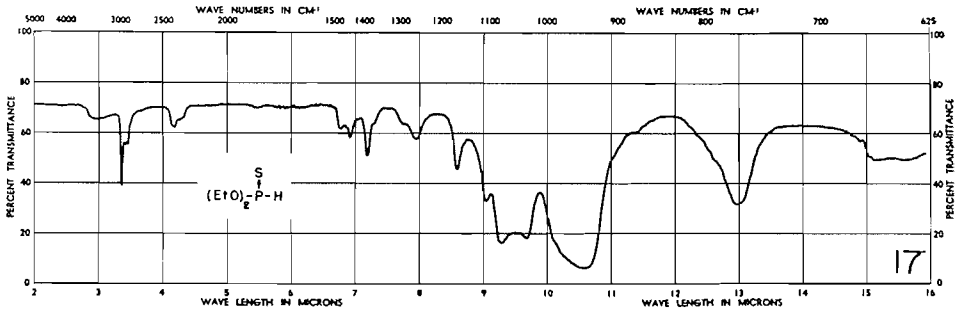

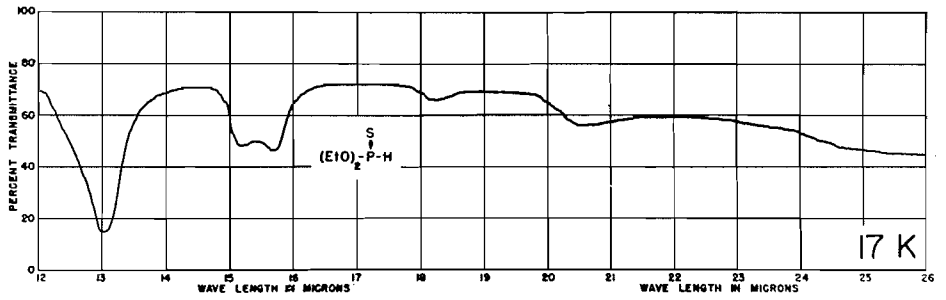

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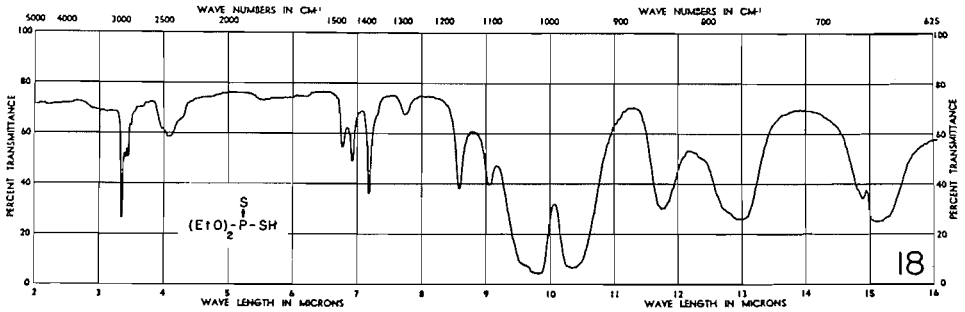

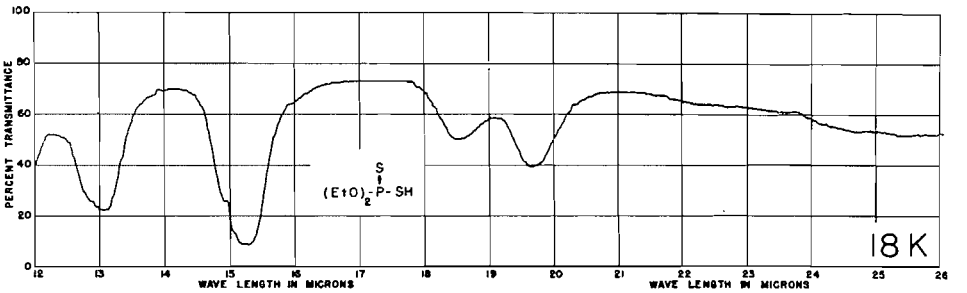

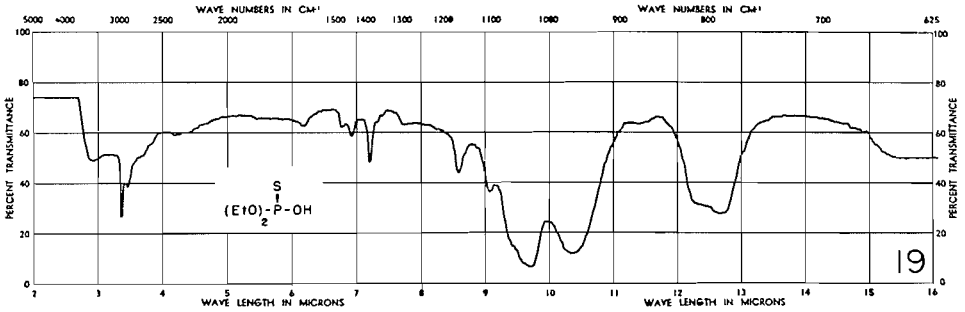

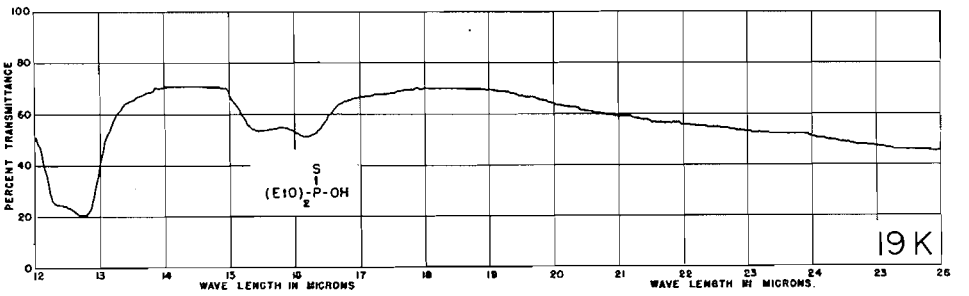

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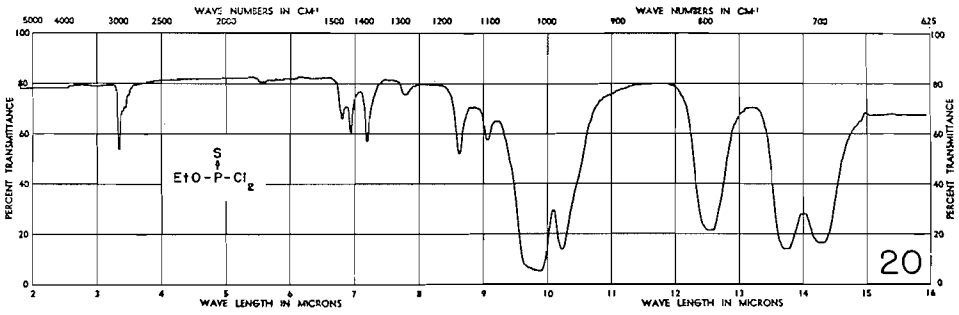

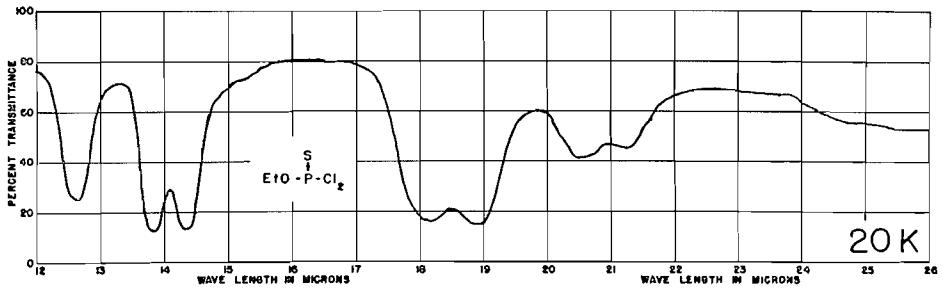

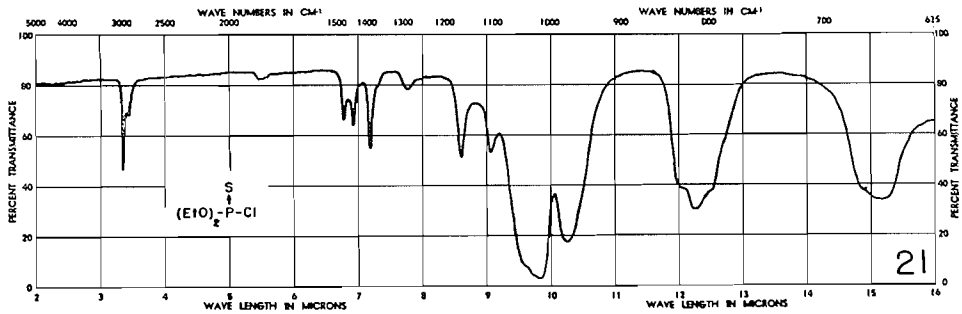

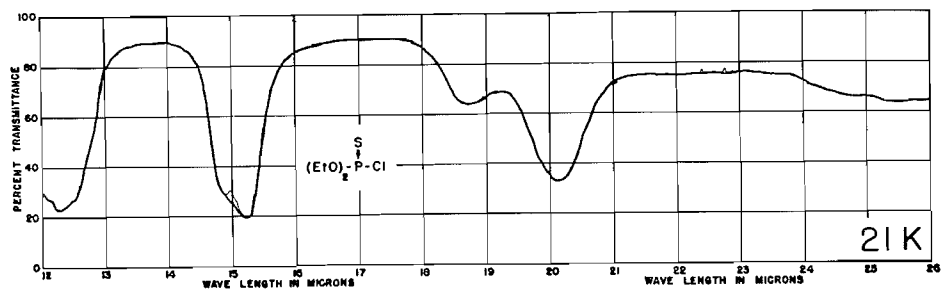

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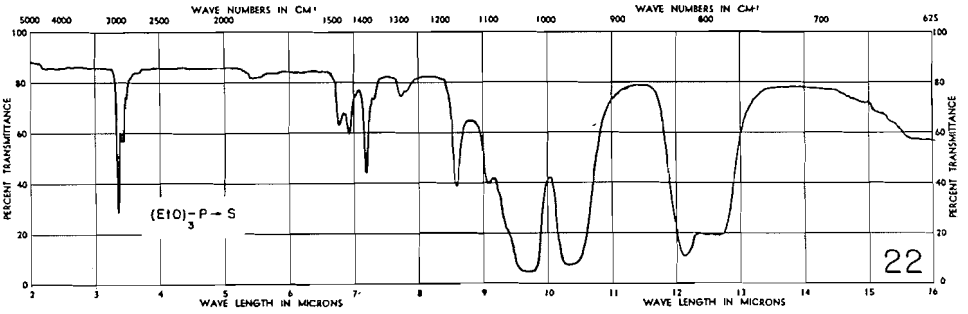

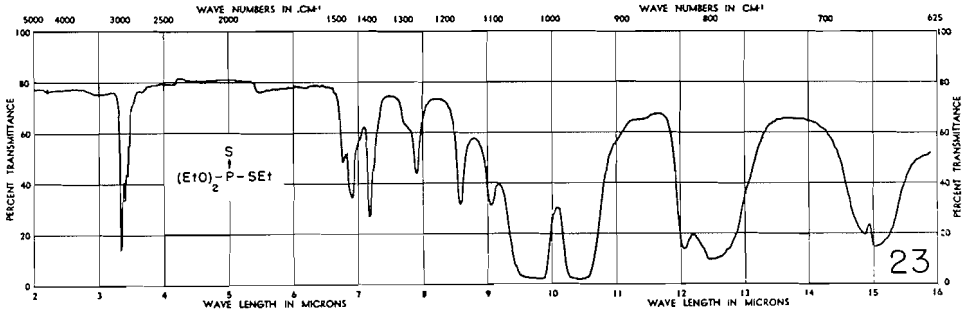

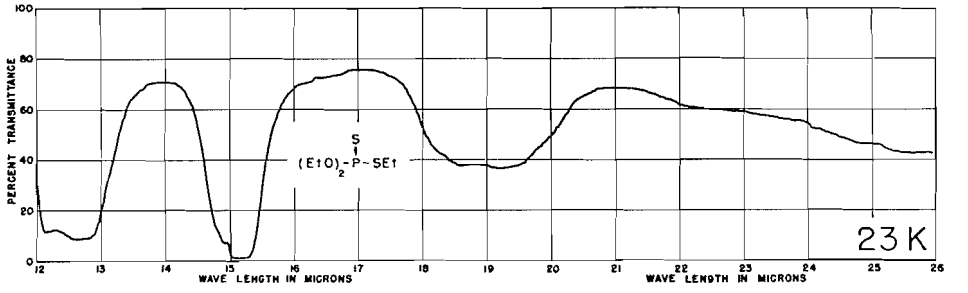

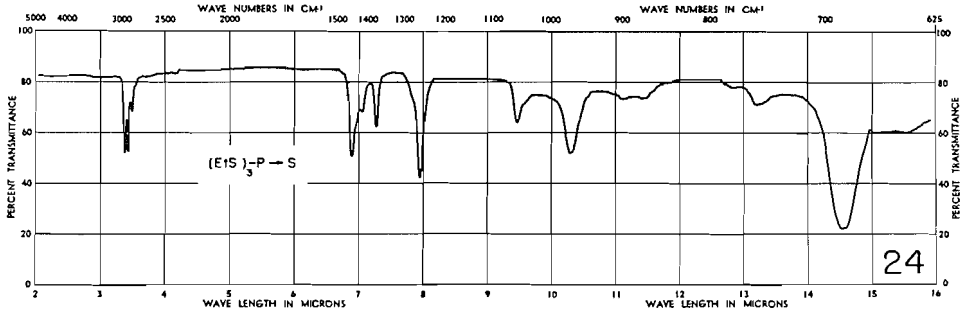

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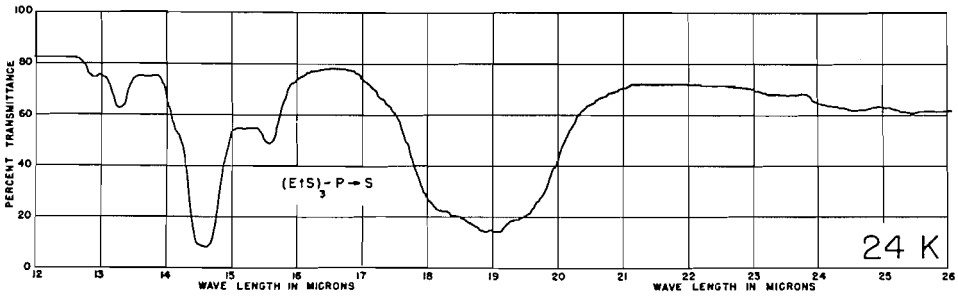

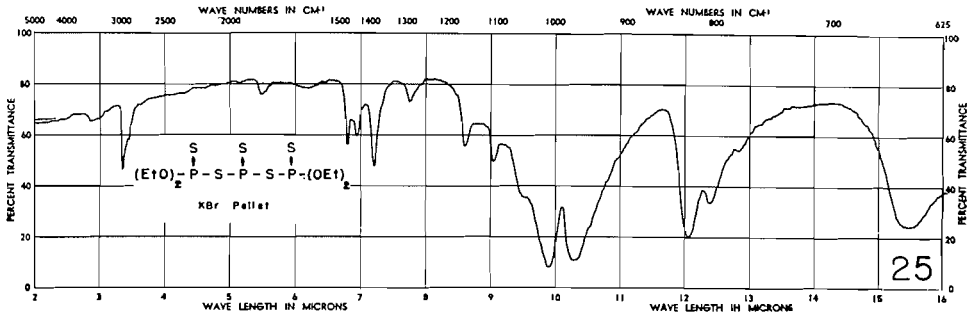

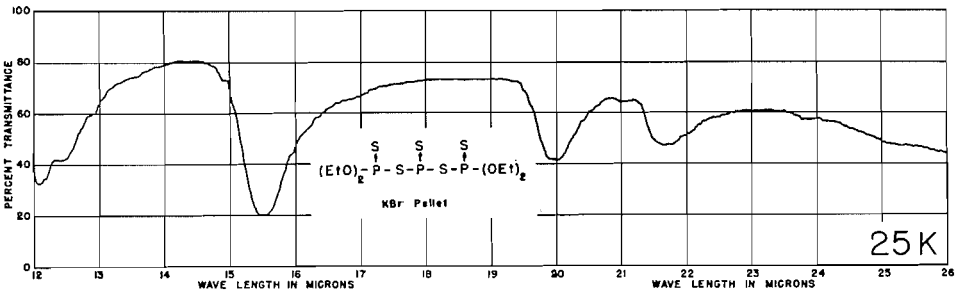

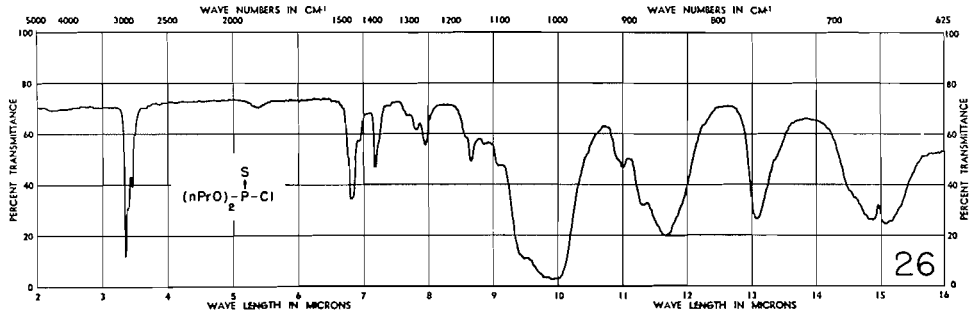

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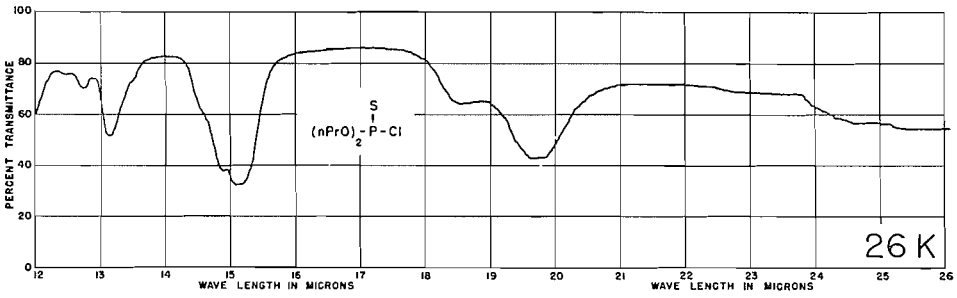

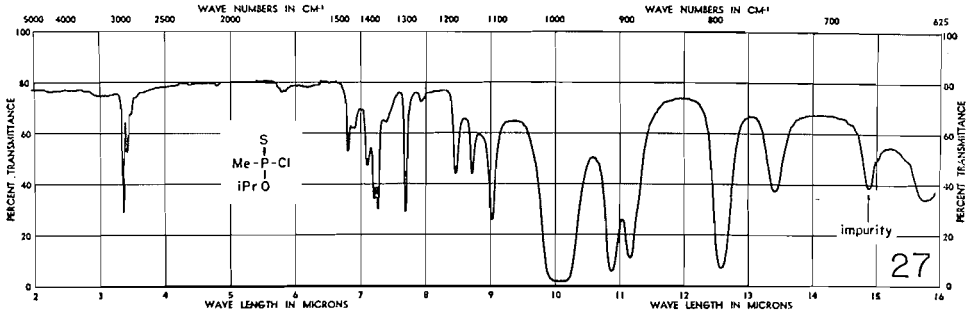

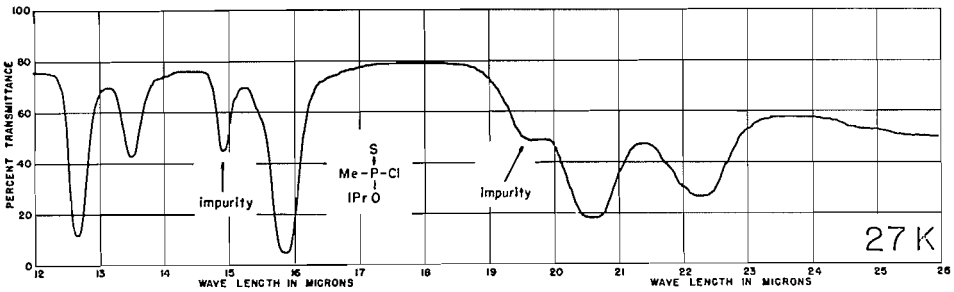

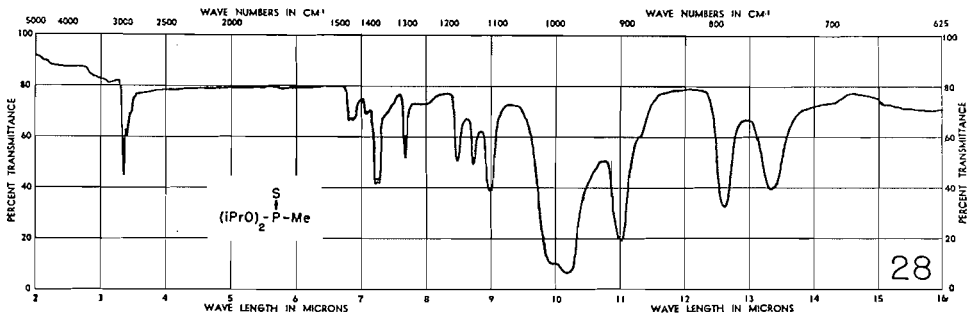

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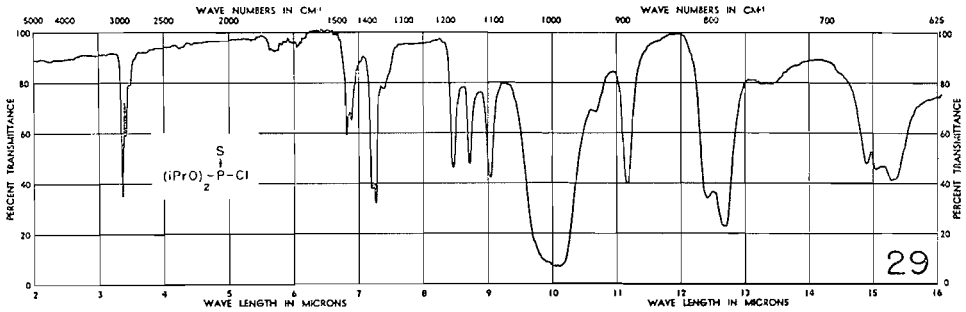

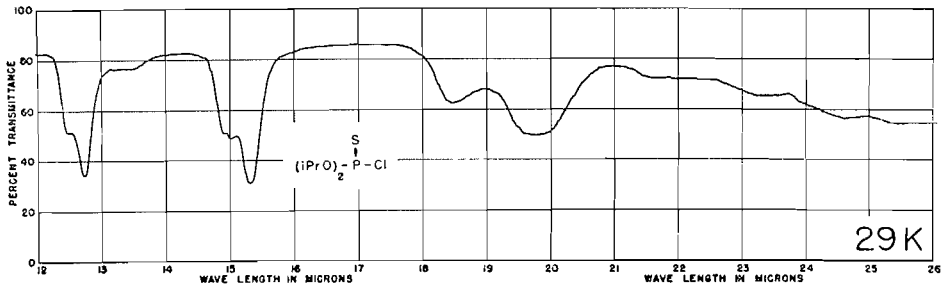

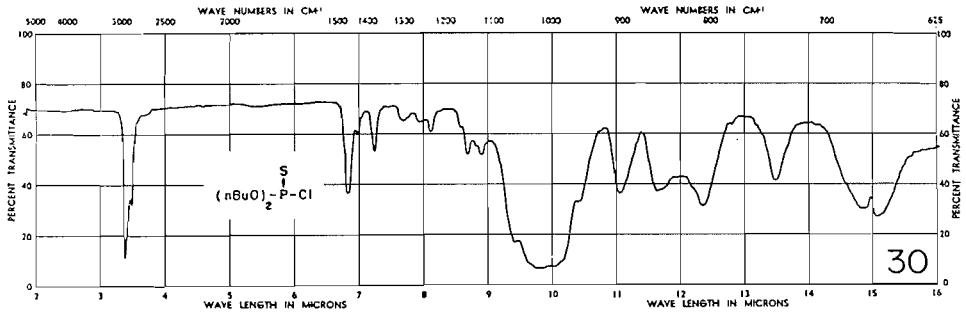

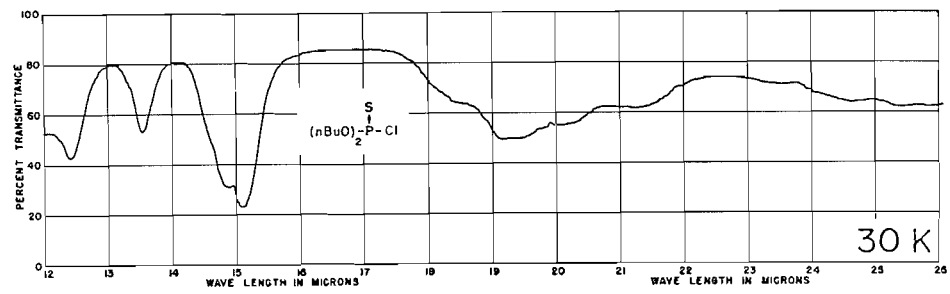

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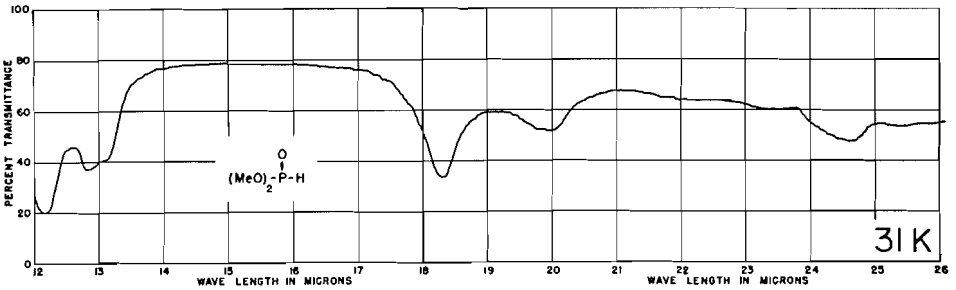

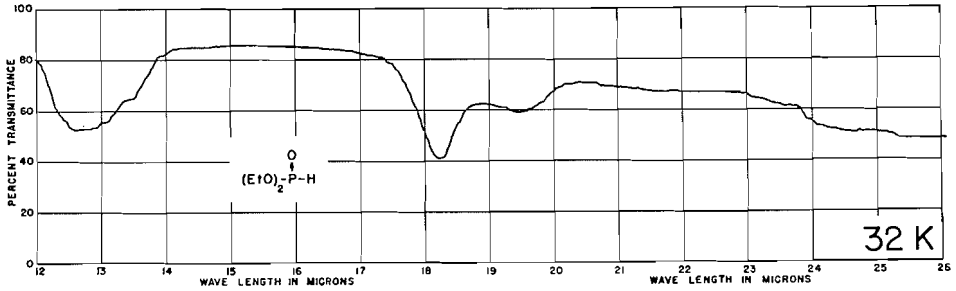

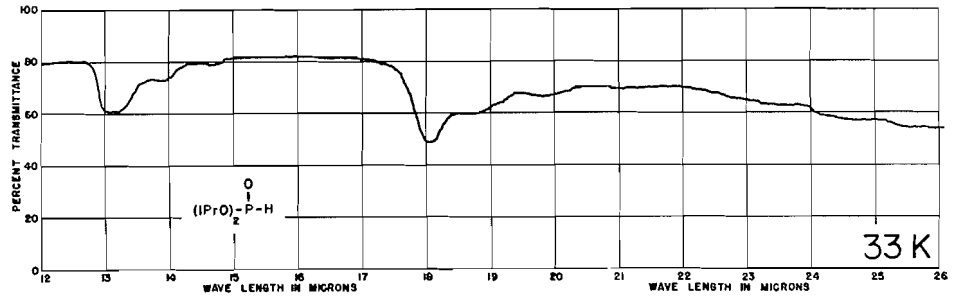

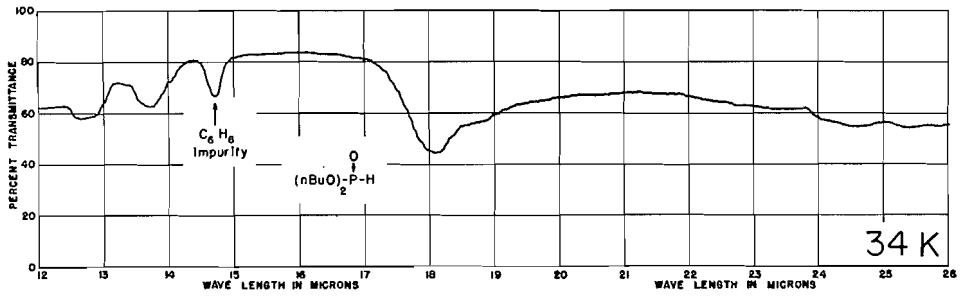

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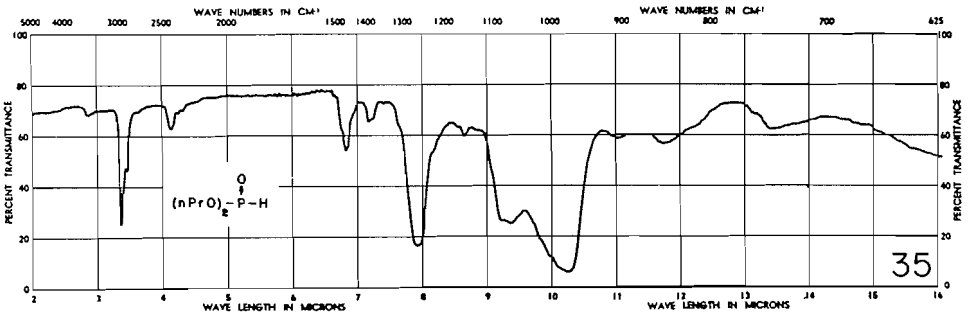

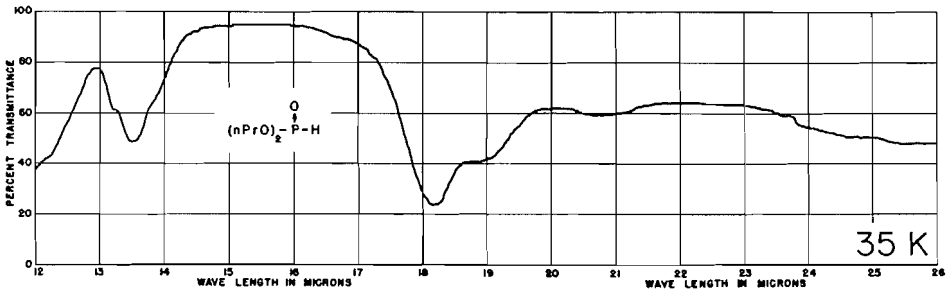

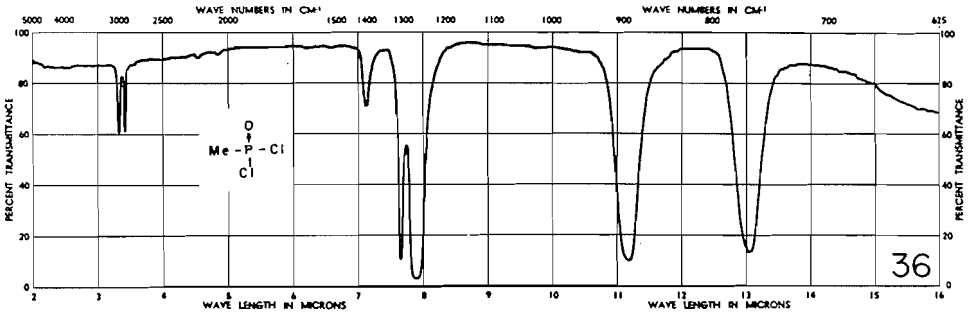

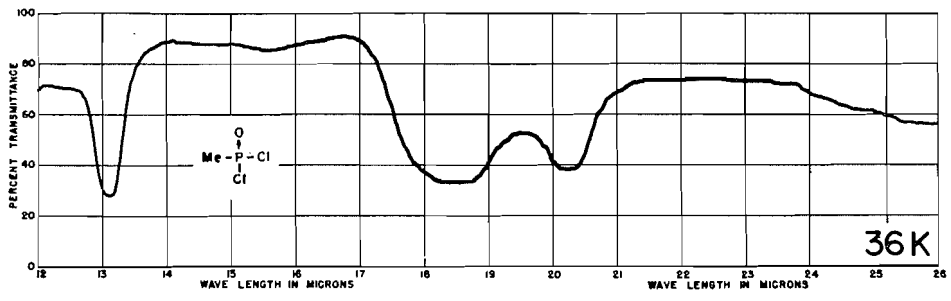

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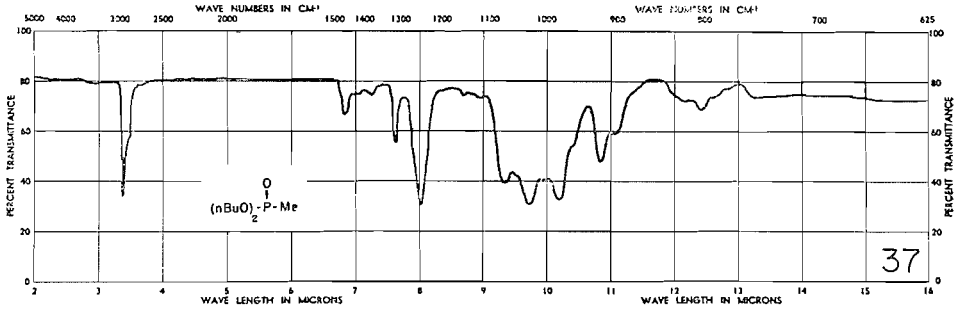

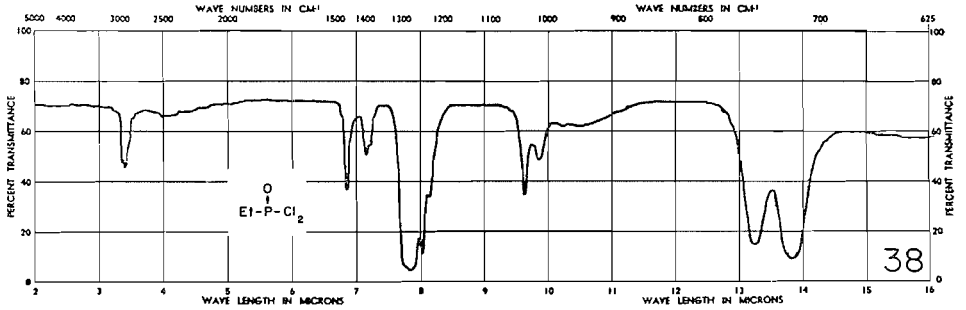

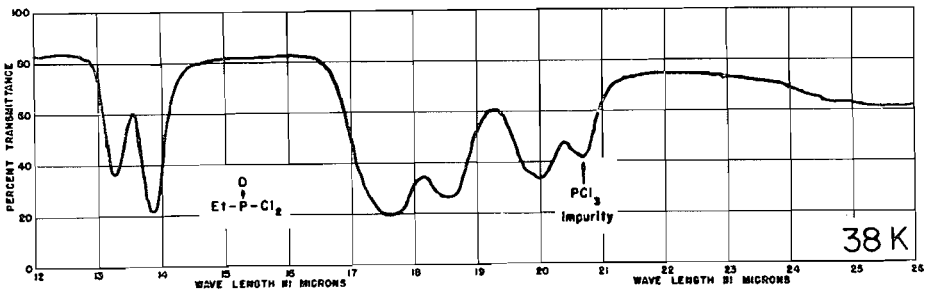

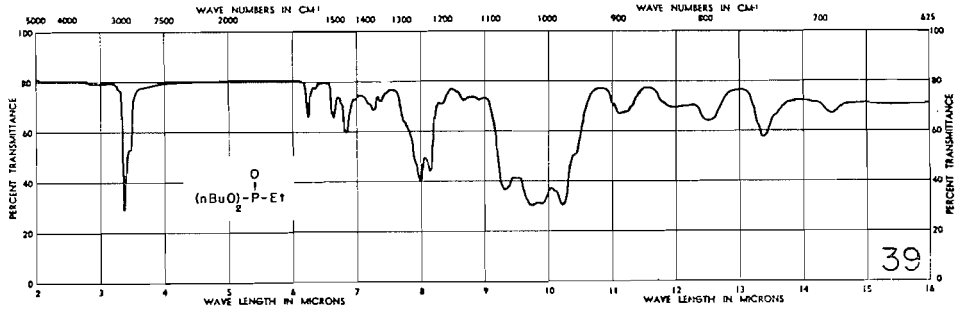

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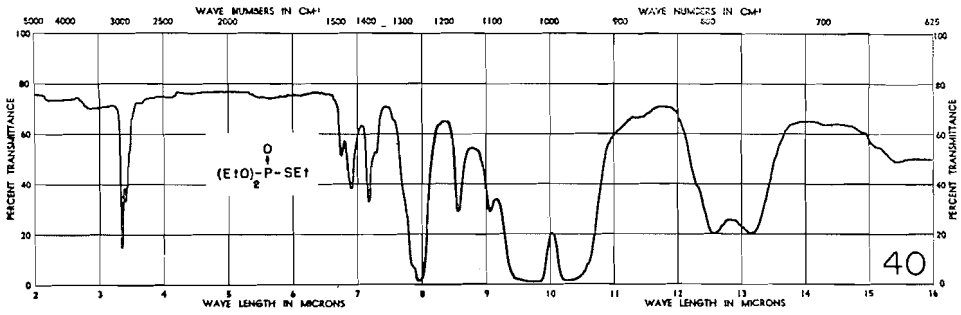

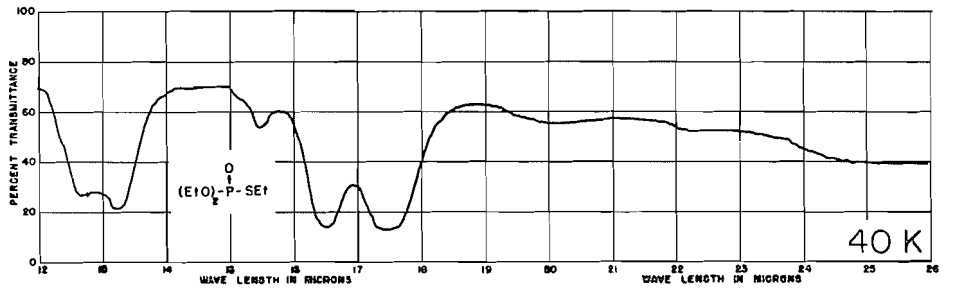

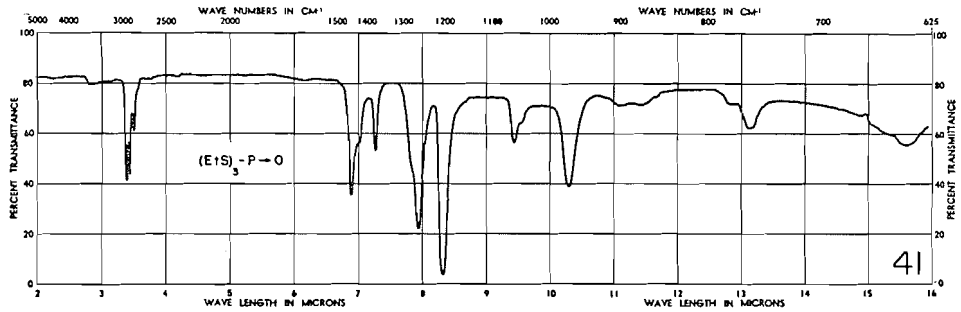

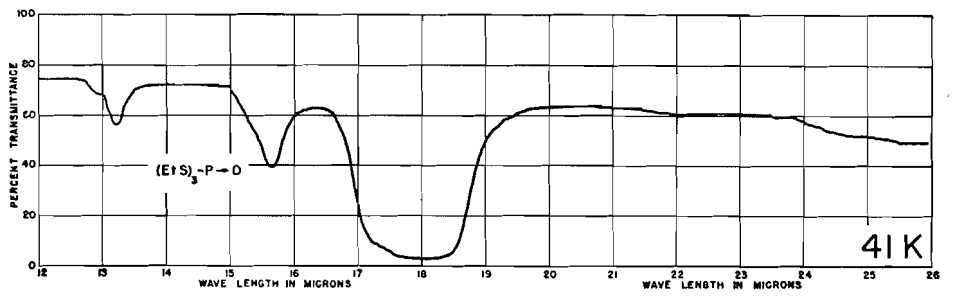

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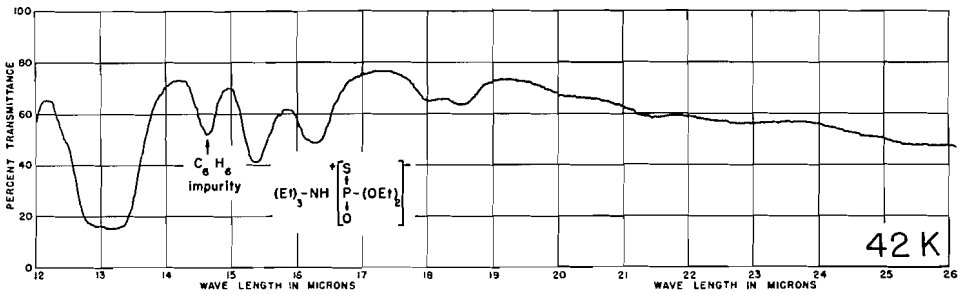

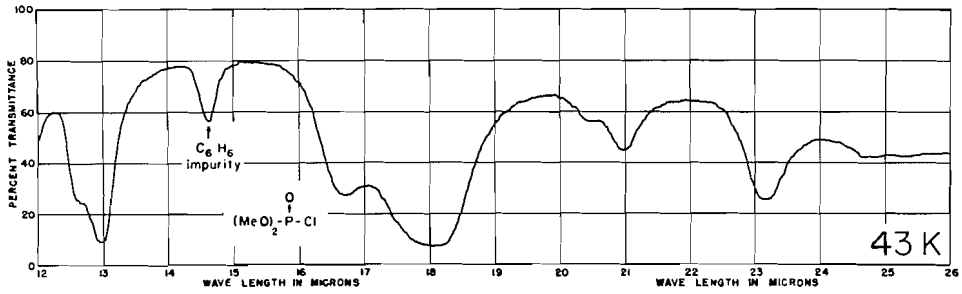

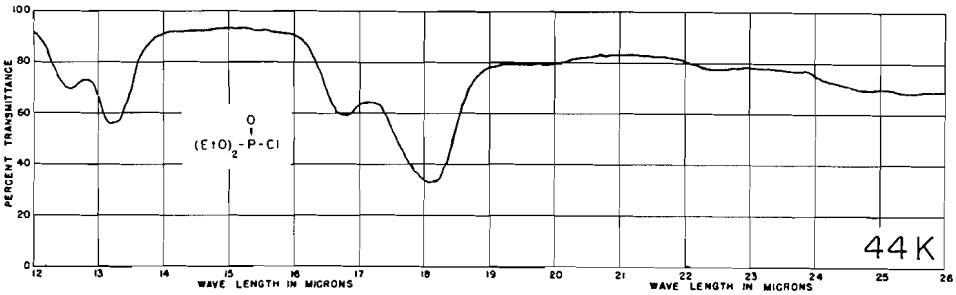

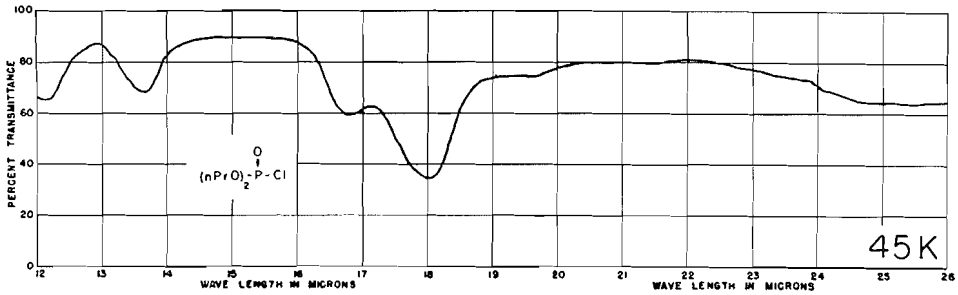

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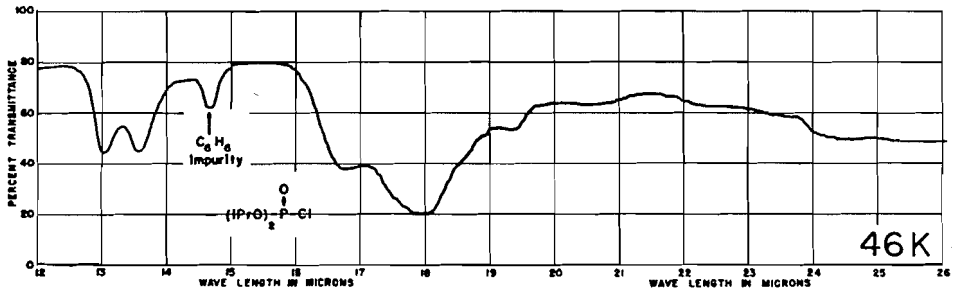

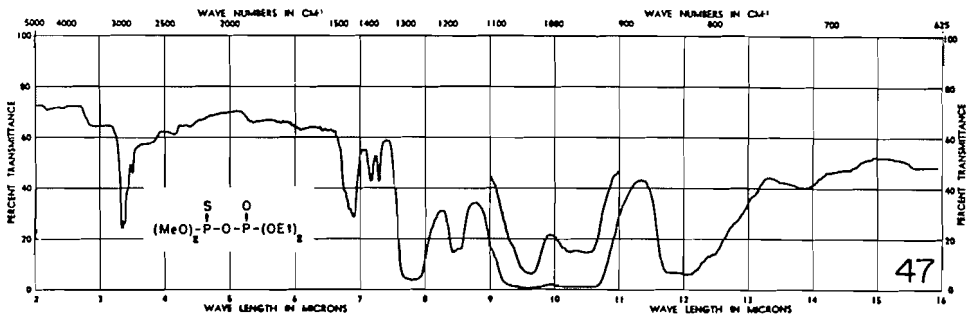

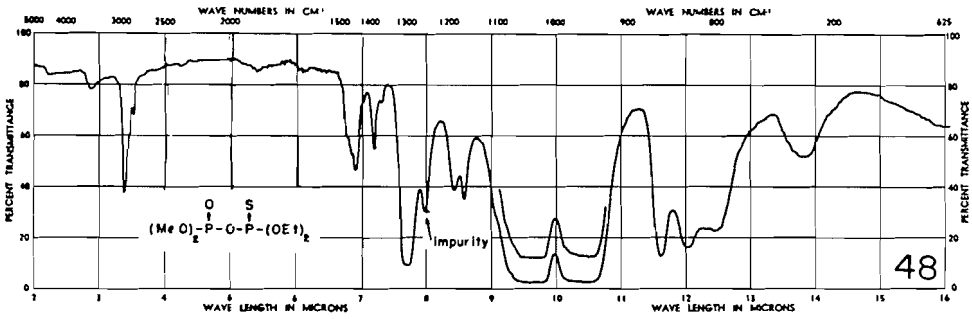

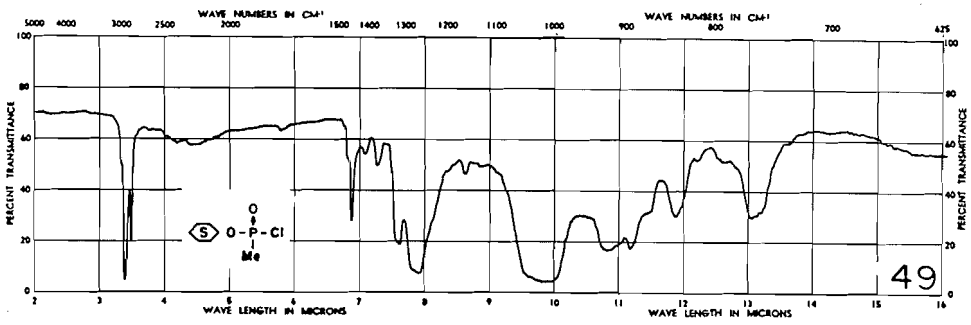

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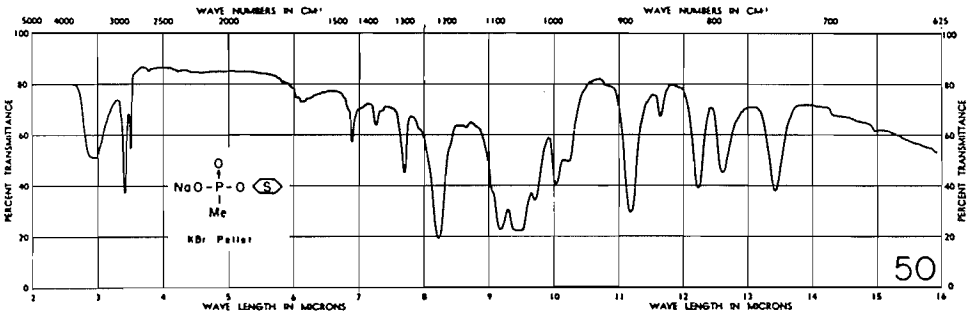

would be expected to have the intense absorption between 9.5 and 9.8 μ and to have its second band nearer 10.4 μ. Reactions (1) and (2) yielded compounds whose spectra were in agreement with the assignments of structures III and IV to the respective products.

The positions actually found are given in Table VII (spectra 47 and 48). Small impurities of the type $(RO)_2$ POSR are still evident.

As further support, compound IV has a sharp band near 11.6 μ found in most $(MeO)_2$ P(O) compounds but not in $(MeO)_2$ P(S) compounds, where it is probably merged with the P(S) absorption near 12.0 μ. This band is absent in compound III.

RÉSUMÉ

Les attributions pour les bandes d'absorption dans l'infra-rouge de plusieurs composés aliphatiques phosphorés sont résumées et étendues. En particulier, les bandes données par les groupements P—O—P, P → S, P—SH, PSR, PH, et PCl sont discutées. Nous avons proposé quelques nouvelles attributions, surtout entre 12 et 24 microns. Deux examples de l'application de ces attributions à la détermination de structure des thiopyrophosphates sont donnés. Nous avons démontré que toutes les méthodes pour la préparation des monothionopyrophosphates donnent exclusivement l'isomère thiono.

ACKNOWLEDGMENT

The authors wish to express their appreciation to Messrs. R. A. Hinge and A. Grey for technical assistance. They are also deeply indebted to Miss R. Parks for the photographs of the spectra.

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THE BIOGENESIS OF ALKALOIDS

XVI. HORDENINE METABOLISM IN BARLEY[1]

By Arlen W. Frank[2] and Léo Marion

ABSTRACT

Hordenine-α-C^{14} fed to sprouting barley was metabolized in the roots. Exhaustive fractionation of extracts from the dried roots yielded several substances of which only the hordenine, N-methyltyramine, and lignin were radioactive. Phenylalanine and tyrosine were inert. The results show that the methylation of tyramine to hordenine is at least partly reversible, but that the hordenine does not revert to tyrosine or phenylalanine. They also indicate that hordenine or N-methyltyramine become incorporated into the lignin.

It has been established previously that both N-methyltyramine and hordenine, occurring in the roots of germinating barley, originate from the precursor tyrosine (14, 15). The amino acid is first decarboxylated and the resulting tyramine is methylated via methionine to N-methyltyramine and to hordenine (12). According to Raoul (19) and others (6, 27), the alkaloids are present in barley during only approximately 30 days. The concentration of alkaloids starts at zero, since none are present in the seed, reaches a maximum at about 11 days of growth, and gradually decreases to zero after one month. This can be interpreted as meaning that during the first 11 days the rate of synthesis of the alkaloids is greater than the rate at which it is used up, whereas after that period it is degraded at a faster rate than it is formed. It was of interest, therefore, to investigate the transformation of hordenine in the plant.

It has been suggested by Raoul (19) on the basis of *in vitro* experiments performed under supposedly physiological conditions that hordenine is demethylated in the plant to tyramine. The same author also investigated the recarboxylation of the demethylated product, but failed to find proper *in vitro* methods under which this step could take place. It has also been assumed (12) that hordenine could undergo further methylation to the quaternary base candicine, which occurs together with hordenine in *Trichocereus candicans* Gillis (20) and *T. lamprochlorus* (16), but these suggestions have never been verified experimentally in the plant, and no candicine has been detected in barley.

Investigations of the behavior of hordenine toward isolated enzymes have shown that whereas tyrosine is converted by tyrosinase to melanin (4, 9, 19) hordenine is not, because of the substitution on the nitrogen. The product of the oxidation of hordenine by a preparation from Scotch broom containing tyrosinase has been identified as *o*-hydroxyhordenine (3). The presence of tyrosinase in barley has been reported by several investigators (9, 19, 25), but James has recently proved that the enzyme does not occur in the rootlets, at least until the 11th day of germination (11). If, therefore, the conclusion that

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[2]*National Research Council of Canada Postdoctorate Fellow, 1954–1955.*

the tyrosinase occurs in some parts of the seedling other than in the rootlets is warranted, the presence of N-methyltyramine and hordenine in the rootlets can be explained. In the absence of tyrosinase, decarboxylation becomes the major pathway of tyrosine metabolism, and the product, tyramine, is methylated to form the alkaloids. This would account for the presence of hordenine solely in the roots, although tyrosine as shown by Raoul (19) is plentiful in the grain at the beginning of germination.

Certain microorganisms convert hordenine to *p*-hydroxyphenylethanol (5), while animal livers have been shown to transform hordenine, N-methyltyramine, and tyramine to *p*-hydroxyphenylacetic acid (7) and to *p*-hydroxyphenylethanol (18). These reactions have all been ascribed to oxidative deamination by the enzyme tyramine oxidase (21), but the presence of this enzyme in barley has not been demonstrated.

In the present work we have attempted to trace the path of hordenine metabolism in barley by feeding hordenine-α-C^{14} to the seedlings and following the radioactivity through an exhaustive fractionation.

EXPERIMENTAL

Hordenine-α-C^{14}

Tyramine-α-C^{14} hydrochloride prepared as previously described (13) was dissolved in aqueous ammonia and the solution extracted with ether in a continuous extractor for 72 hr. The ether extract was evaporated and the residual oily base distilled, b.p. 120–130° at 0.01 mm. The base (137 mgm., 1.0 millimole), with a specific activity of 1.15×10^7 disintegrations per min. per millimole,[3] was methylated with formic acid and formaldehyde as described by Raoul (19). The hordenine-α-C^{14} thus obtained was sublimed at 120–130° at 0.01 mm., wt. 70.4 mgm. (44% yield). A paper chromatogram showed that tyramine and N-methyltyramine were absent from the product. It had a total activity of 4.77×10^6 d.p.m., and a specific activity of 1.12×10^7 d.p.m. per millimole.

Administration of Hordenine-α-C^{14} to Barley

Barley (Charlottetown No. 80, 720 gm. dusted with the fungicide Semesan) was grown as previously described (13) except that the seeds were spread on glass wool to minimize the growth of mold. The seeds were about two years old and had lost some of their germinative capacity (35–40% germination). On the sixth day of sprouting the barley was fed (as previously described (13), by addition to the germination trays) a solution of hordenine-α-C^{14} (70.4 mgm.) in water (600 ml.) containing concentrated hydrochloric acid (0.10 ml.). The administration of the alkaloid had no apparent ill effect on the growth of the barley. On the 11th day of sprouting the shoots were clipped off as near as possible to the root mat and dried at 70°, wt. 32 gm., and total activity less than 0.3×10^5 d.p.m. The glass wool mats containing the roots were dried at 110° without separation.

[3]*The activities were determined as thin samples with a Radiation Counters Laboratory "Nucleometer" making the usual corrections for self-absorption, etc.*

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Extraction of Roots

The mats consisting of glass wool and the roots were cut into strips and extracted with methanol for 48 hr. The extract after evaporation of the methanol weighed 6.09 gm. and had a total activity of 1.01×10^6 d.p.m. (i.e., 21% of the activity of the hordenine fed to the barley). The roots were now extracted with three portions of 0.5 *N* sodium hydroxide by successive boiling for eight hours and filtering (1). After this treatment the roots were inactive. The three alkaline extracts had the following activities: 3.0×10^6, 6.3×10^5, and less than 0.3×10^5 d.p.m. respectively, totalling 76% of the activity administered. The sum of the activities of all the extracts amounted to 97% of the activity administered as labelled hordenine.

The methanol extract was suspended in water to which was added enough hydrochloric acid to make it acid to Congo red, and the mixture extracted with ether. The aqueous liquor was then treated as described previously (13) to isolate the hordenine (116.3 mgm., specific activity, 8.58×10^5 d.p.m. per millimole) and the N-methyltyramine (34.9 mgm., specific activity, 1.43×10^5 d.p.m. per millimole). Choline was separated from the liquor from which the alkaloids had been removed, via the reineckate by the usual method (12, 15), and isolated as the chloroplatinate. It was inactive. No candicine was present.

Fractionation of the Sodium Hydroxide Extract

The three sodium hydroxide extracts were filtered and acidified separately with 5 *N* sulphuric acid. Precipitates were formed in the first two only (Residue B). The two filtrates were combined with the clear extracts and the combined liquor concentrated to 3 liters, alkalized to litmus with sodium hydroxide, and neutralized with acetic acid. A gelatinous precipitate settled out which was removed by centrifugation (Residue C). The mother liquor was then freed of much of the salt it contained by alternate precipitation with ethanol and concentration. The precipitates were combined with Residue C. After this treatment the aqueous solution D measured 800 ml., was slightly acid to litmus, and had an activity of 8.28×10^5 d.p.m.

One quarter of this solution D was percolated through a cation exchanger (Dowex 50-X4, hydrogen form, chloride-free) and an anion exchanger (Amberlite IR-4B, hydroxyl form, neutral to litmus) contained in columns (40 cm. $\times$3.5 cm.) connected so that the effluate from the cation exchanger passed directly into the anion exchanger. Water was percolated through the assembly until 2 liters of percolate had been collected. The percolate included sugars and other neutral substances which were negligibly radioactive (less than 1.0×10^4 d.p.m.). The columns were disconnected and washed separately with 1 liter of water (washings inactive). The anion exchanger was then eluted with 3 liters of 0.2 *N* hydrochloric acid, giving 1.604 gm. of acids, also negligibly radioactive (less than 2×10^3 d.p.m.). Elution of the cation exchanger with 1 liter of 0.15 *N* ammonia gave a basic fraction (0.990 gm.) with an activity of 6.1×10^4 d.p.m. No further activity was detected on further elution with ammonia or with 0.1 *N* sodium hydroxide.

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Fractionation of the Weak Bases

The radioactive eluate from the cation exchanger contained principally the weakly basic amino acids and gave a positive Millon test. It was chromatographed on a charcoal column (2 cm.×9 cm.) (22). The charcoal (Darco G-60, 5 gm.) was pretreated by being heated on the steam bath with 200 ml. of 20% acetic acid, was cooled and washed on a filter with water, and then was transferred to the column in a slurry with 5% acetic acid. The residue left after evaporation of the eluate from the cation exchanger was dissolved in 5% acetic acid (100 ml.) and the solution transferred to the column, which was later eluted with 5% acetic acid until 300 ml. of eluate had been collected. This eluate on evaporation *in vacuo* yielded the non-aromatic amino acids (1.545 gm., activity, 2500 d.p.m.). The charcoal column was further eluted with 300 ml. of a mixture of water, glacial acetic acid, and phenol in the proportion of 80:20:5 (22). This eluate was extracted with ether to remove the phenol and evaporated to dryness under diminished pressure, leaving a residue of aromatic substances (0.198 gm., activity, 5.9×10^4 d.p.m.). A paper chromatogram of the residue developed with 80% phenol and sprayed with ninhydrin showed that it contained phenylalanine and tyrosine, but no tryptophan.

Phenylalanine and Tyrosine

The aromatic fraction described above was dissolved in a small volume of 4 *N* hydrochloric acid, transferred to a column (1 cm.×50 cm.) of Dowex 50-X12 prepared according to Wall (28), and eluted with 4 *N* hydrochloric acid. The eluate was collected in 5 ml. fractions, and aliquots were chromatographed on paper to spot the amino acids, which were detected with ninhydrin. Fractions 20–48 and 54–84 contained tyrosine and phenylalanine respectively. Each of these two acids was dissolved in 5% acetic acid (5 ml.) and the solution percolated through columns of Dowex 1-X8 in the acetate form to convert the hydrochloride to the free bases (10). The two eluates (each 50 ml.) were evaporated to dryness. Neither the tyrosine (43.9 mgm.) nor the phenylalanine (53.4 mgm.) after recrystallization was radioactive.

Hordenine and N-Methyltyramine

The mother liquor from the first phenylalanine crystallization and fractions 85–154 from the Dowex 50–X12 column gave a strong Millon test. A paper chromatogram under conditions previously described (13) showed the presence of hordenine and N-methyltyramine, but no tyramine nor tyrosine. The combined fractions 85–154 (activity, 4.3×10^4 d.p.m.) were alkalized with ammonia and extracted with ether for 48 hr. The extract (activity, 3.3×10^4 d.p.m.) contained hordenine and N-methyltyramine. The alkaloids were isolated directly from the remaining three-quarters of solution D by alkalizing the solution with ammonia and extracting with ether in the usual manner. To this extract were added the bases obtained above and the solution chromatographed on alumina to separate the two alkaloids. After sublimation the hordenine weighed 22.8 mgm. and had the specific activity 6.28×10^5 d.p.m. per millimole, and the N-methyltyramine weighed 32.2 mgm. and had the specific activity 1.5×10^5 d.p.m. per millimole.

Lignin

Residue B (activity, 1.95×10^5 d.p.m.) was treated by the procedure of Bondi and Meyer (1) in order to isolate the lignin. The product, a brown amorphous powder weighing 0.704 gm., had a total activity of 0.96×10^5 d.p.m. or 136 d.p.m. per mgm. Found: ash, 1.47%; N (ash-free), 5.81%; OCH_3 (ash-free), 4.53%.

A sample of this lignin was oxidized with nitrobenzene and alkali as described by Stone and Blundell (26). A product was obtained which gave a brick-red derivative with 2,4-dinitrophenylhydrazine. This derivative was completely inactive, but could not be crystallized and was not further identified.

A further quantity of lignin was isolated from Residue C. This residue consisted of dark brown gelatinous material and salts. It was taken up in water (1 liter) and dialyzed for one week to remove the salts and any remaining substances of low molecular weight. The amorphous, insoluble material was collected by centrifugation, and stirred in 1.25 *N* sodium hydroxide (500 ml.). The alkali-soluble material was treated as before (1) and yielded 1.670 gm. of brown amorphous powder with an activity of 2.1×10^5 d.p.m. or 126 d.p.m. per mgm. No proof of the identity of the two lignin preparations was possible, but the activities per mgm. are in good agreement.

DISCUSSION

Since the methanol and the sodium hydroxide extracts together accounted for 97% of the activity fed to the plant as labelled hordenine, any loss to the air as carbon dioxide was negligible, and it appeared probable that hordenine was not degraded to one-carbon fragments, except for the methyl group. The only compounds isolated that were radioactive were hordenine, N-methyltyramine, and lignin. Hordenine was not broken down to fragments capable of taking part in sugar synthesis, for the sugars were inert. Phenylalanine and tyrosine were also inert, and no tyramine was present. Consequently hordenine seems to undergo a partial demethylation only, giving rise to N-methyltyramine. No recarboxylation of the bases back to amino acids takes place since the amino acids isolated were not radioactive.

It has been shown by Freudenberg and Bittner (8) and by Siegel (23) that simple C_6, C_3 compounds can be lignin precursors. More recently Siegel (24) has demonstrated that in the presence of cellulose, eugenol is converted by peroxidase – hydrogen peroxide to a polymeric substance giving positive color tests for lignin. Also, Brown and Neish (2) have shown that C_6, C_3 amino acids such as phenylalanine and tyrosine do act as lignin precursors.

It is known that the lignin of very young plants unlike that of older plants contains nitrogen which appears to be an integral part of it. The lignin of two-week-old barley seedlings has been stated to contain as much as 8% nitrogen by Phillips (17), who further showed that the nitrogen content fell steadily as the plants matured.

The isolation of radioactive lignin in the present investigation, where the

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only source of C^{14} was the hordenine, indicates that a C_6, C_2 fragment can also take part in lignin synthesis. The results also lead to the inference that hordenine is the source of at least part of the nitrogen in barley lignin. This inference, however, can only be drawn with caution and will require more definite proof.

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THE SYSTEM LITHIUM CHLORATE – LITHIUM CHLORIDE – WATER AT VARIOUS TEMPERATURES[1]

By A. N. Campbell and J. E. Griffiths[2]

ABSTRACT

The equilibrium diagram of the system lithium chlorate – water has been determined at all temperatures and that of the system lithium chlorate – lithium chloride – water at the temperatures 3.0°, 6.0°, 8.5°, and 25.0° C.

Lithium chlorate forms three hydrates having the formulae:

(i) $(LiClO_3)_4.H_2O$—stable in contact with solution from 20.5° to 42.0° C.

(ii) $LiClO_3.H_2O$—stable in contact with solution from −0.1° to 20.5° C.

(iii) $LiClO_3.3\ H_2O$—melts congruently at 8.4° C.

Hydrate (i) was discovered by Berg but he gave to it the formula $(LiClO_3)_3.H_2O$.

Lithium chlorate and lithium chloride form no double salts at the temperatures of investigation.

Lithium chlorate exists in two enantiotropic forms, namely the α and the β forms. The transition, $\alpha \leftrightarrow \beta$, takes place at 99.8° C. and the α form has the lower density. The γ form, proposed by Kraus and Burgess, does not exist either stably or metastably. The X-ray diffraction pattern of β-$LiClO_3$ has been obtained.

The question of the number and nature of the hydrates of lithium chlorate, after passing through the usual period of ill-founded claims, was attacked in a systematic manner by Kraus and Burgess (5) and by Berg (1), in the period 1926 to 1929. Almost all of the experimental data of these researches are in good agreement but the authors differ, in some respects, regarding their interpretation. Kraus and Burgess claim the existence of three anhydrous modifications, of a trihydrate, and of a monohydrate. Berg claims only two anhydrous modifications and three hydrates, viz. a hydrate with $\frac{1}{3}$ mole water per mole of salt, a monohydrate, and a trihydrate. In short, the two investigators differ in that Kraus and Burgess claim the existence of a γ-anhydrous form, between 22° and 44° C., where Berg claims a hydrate with $\frac{1}{3}$ mole water; in other respects they agree.

In order to decide the conflicting interpretation given above, as well as to verify the formulae of all hydrates, we decided to add a third ion to the binary system $LiClO_3$–H_2O, and to investigate the system $LiClO_3$–LiCl–H_2O, at various temperatures. Under these circumstances, the Schreinemakers' "wet rest" method determines the composition of all hydrates without ambiguity. In addition, we thought it well to repeat part of the work of Kraus and Burgess and of Berg, on the binary system. We have also made attempts, more or less successful, to obtain X-ray diffraction patterns of the phases in dispute. Finally, we attempted to determine transition temperatures with the dilatometer since this is the most delicate method of determining transition temperatures, but here again we were not entirely successful because of obstinate metastability.

[1]*Manuscript received June 7, 1956.*
Contribution from the Chemistry Department, University of Manitoba, Winnipeg, Manitoba.
[2]*N.R.C. Bursar, 1955–56.*

EXPERIMENTAL

Lithium chlorate was prepared by a method which is essentially that of Potilitzin (6) and of Kraus (5), viz. double decomposition between barium chlorate and lithium sulphate, but the final dehydration to anhydrous salt is a modification of our own. The suppliers' analyses, both of lithium sulphate and of barium chlorate, showed that these salts were very pure; as the method of preparation of the anhydrous salt does not permit recrystallization this is a necessity, as is also the use of exact stoichiometric quantities.

A 1 molar solution of barium chlorate was heated to about 85° C., and a 1 molar lithium sulphate solution was added slowly to this with a dropping funnel until equivalence was reached. The precipitated barium sulphate was removed by repeated filtration. To ensure equivalence of lithium and chlorate ions, the resulting solution was titrated with dilute solutions of barium chlorate and lithium sulphate.

The solution was evaporated slowly, the temperature being kept below 85° C., up to an approximate concentration of 50% lithium chlorate. The filtered solution was transferred to a 250 ml. Claissen flask and dehydration was carried out under a reduced pressure of less than 5 mm. mercury, the distillate being absorbed in concentrated sulphuric acid. The temperature was kept below 85° C., since decomposition begins at this temperature in concentrated solutions. The result of this procedure was a solution containing about 90% lithium chlorate.

On the cooling of the solution to room temperature, the salt crystallized; it was placed under vacuum over phosphorus pentoxide. After about a month, the water content had been reduced to about one per cent. To remove the last trace of water, the salt was placed in a vacuum furnace, over phosphorus pentoxide, and kept at a temperature of 80° C. After several months, no further change was found in the melting point of the salt.

None of the textbook methods for the analysis of lithium chlorate is entirely satisfactory, so we worked out the following method: A weighed sample of lithium chlorate is made up to a volume of 250 ml. A 10, 20, or 25 ml. aliquot is transferred to a 250 ml. iodine flask. To this is added 40 ml. concentrated orthophosphoric acid, followed by the addition of about 0.1 gm. sodium carbonate, to exclude air from the flask. Approximately 25 ml. of iodate-free potassium iodide solution (0.2 gm./ml.) is added and the stoppered flask allowed to stand at room temperature for 60 to 70 min. The free iodine is titrated with sodium thiosulphate. Standardization of the method with pure sodium chlorate indicated an accuracy of $\pm 0.4\%$.

The chloride content of solutions containing appreciable amounts of chloride was determined volumetrically with silver nitrate solution, using an alcoholic solution of sodium dichlorofluoresceinate as indicator (4). For solutions containing less than five per cent chloride the standard gravimetric method was used.

Solubility determinations were made in the usual way. For temperatures below room temperature a cooled and controlled thermostat was used. Temperature control was good to ± 0.05° C. throughout this research

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Thermal analysis was used only for the ice curve, the binary eutectics, and $\alpha \leftrightarrow \beta$ transition. After a break had occurred on the cooling curve, a sample of the equilibrium mother liquor was removed for analysis. Temperature was measured with an iron–constantan thermocouple and a good potentiometer.

The technique of X-ray diffraction measurements is now standard but, in the case of anhydrous lithium chlorate, measurements were rendered difficult by the very hygroscopic nature of the substance (it is comparable with that of phosphorus pentoxide). A sample of the anhydrous salt was ground to a fine powder and then returned to the vacuum desiccator and redried for several days. Following this, a very fine and thin-walled capillary tube (outside diameter 0.5 mm. and inside diameter 0.3 mm.) was filled with the sample and immediately sealed at both ends. The intensities of the lines were estimated visually. Powder photographs were taken of a sample that had been in a vacuum desiccator at room temperature for seven months and which we therefore considered to be the form stable at room temperature. A quantity of the same substance was then placed in another vacuum desiccator, held at 80° C. for a week, and then photographed: the results obtained were the same as for the unheated sample.

By means of a high temperature X-ray camera, we were able to take X-ray patterns at 115±5° C. We supposed that, at this temperature, the anhydrous lithium chlorate would have transformed to a different allotrope which would exhibit a different pattern. The result was disappointing; as far as could be judged, the pattern was the same as that at room temperature but the weaker lines of the room temperature picture had vanished and the few lines which did appear were quite broad. This is what would be expected if the lattice structure were the same. The atoms of the lattice would have increased thermal vibration at the higher temperature. A sample of the anhydrous lithium chlorate was sent to the National Research Council at Ottawa for further X-ray study. The work was carried out by Dr. L. D. Calvert, who was able to obtain diffraction patterns of the β form up to the melting point of the salt. Dr. Calvert was unable to detect any change in lattice structure corresponding to the change from the β to the α form, but his apparatus was not susceptible of close temperature control. At higher temperatures, however, he was able to evacuate his camera and this reduces the absorption of X rays by the air. The capillaries used in his work had a wall thickness of 0.007 mm.

The dilatometric work was carried out much in the usual manner. The bulb of the dilatometer had a stoppered side-tube to facilitate filling. The dilatometer was filled in a dry-box. About 100 gm. of anhydrous lithium chlorate, which had been dried for five months, was used to fill the bulb to about three-fourths capacity. The indicator liquid was *p*-xylene which had been dried over sodium for three days. The bulb of the dilatometer was placed in a thermostat whose temperature was constant to ±0.1° C. The temperature was raised one degree every 24 hr., but in the range 35° to 50° C., where Kraus and Burgess have claimed an allotropic transformation (5), the rate of increase was reduced to 0.5° per 24 hr. No break occurred on the curve of capillary height versus temperature, up to 106° C., with rising temperature. Since it was still

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possible that a very slow transition had been overlooked, the temperature was kept at 60° C. for a week but there was still no indication of an $\gamma \rightarrow \beta$ transition. At higher temperatures an $\alpha \rightarrow \beta$ transition occurred and this was reversible. The formation of the α modification from the β modification is accompanied by a marked expansion but the change, in both directions, showed marked hysteresis.

THE SYSTEM LITHIUM CHLORATE – WATER

Since the part of the diagram where ice and solution were in equilibrium was of little interest, this was outlined by the method of thermal analysis. The compositions of the solutions in equilibrium with ice at various temperatures were determined by chemical analysis. With the exception of a few fixed points the rest of the equilibrium diagram was investigated by isothermal solubility determinations. The solubilities covered the range of composition

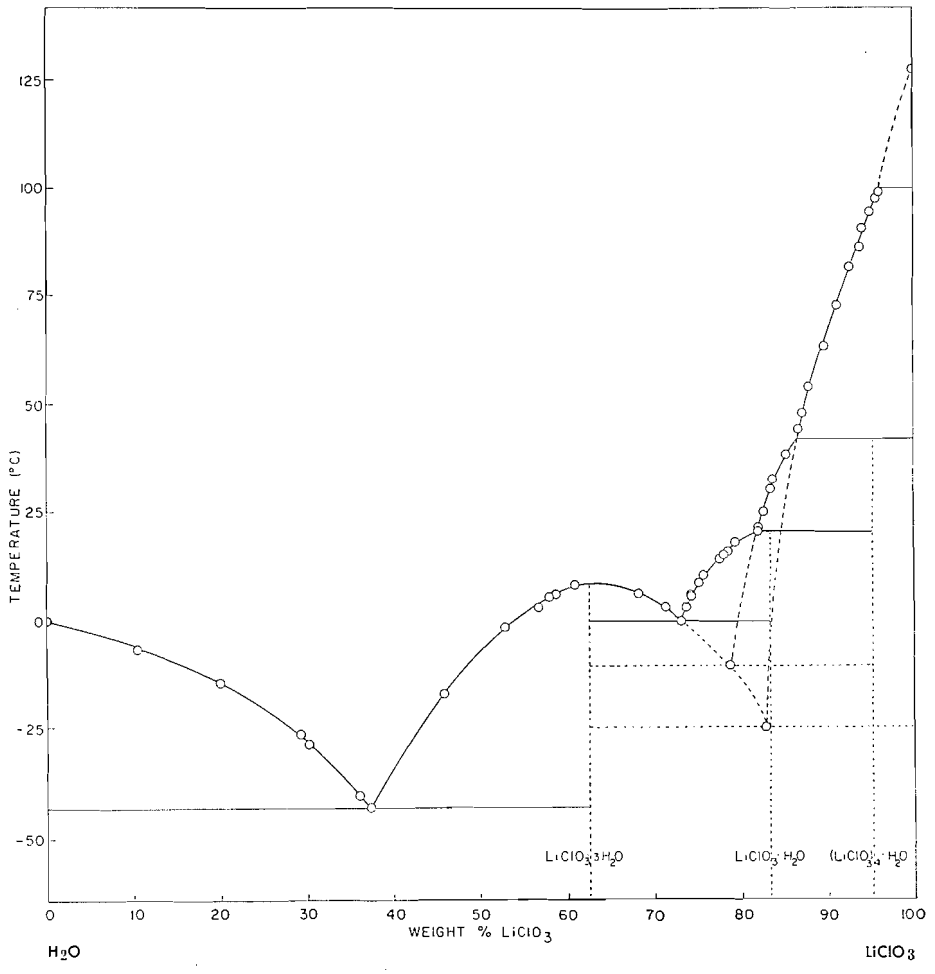

FIG. 1. System $LiClO_3$–H_2O.

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from 45.8 to 95.5 weight per cent lithium chlorate. The upper temperature reached was 98.9° C. The determinations were discontinued at this point because the change of solubility per degree rise in temperature had become less than the accuracy of the analysis.

The stable and metastable binary eutectics were determined by thermal analysis in the usual way. The thermal analysis of the anhydrous salt was conducted in an evacuated vessel, with a copper–constantan thermocouple and a Minneapolis–Honeywell recording potentiometer. The temperature was raised slowly to a temperature above the melting point and the melt then allowed to cool slowly. The experiment was repeated many times in the vicinity of 40° C., because of the $\beta \leftrightarrow \gamma$ transition which is said to occur there.

EXPERIMENTAL RESULTS

The solubility relations and the results of thermal analyses are reported in Table I, together with the method used to arrive at them. The equilibrium diagram is shown in Fig. 1. The broken lines indicate solubility curves in the metastable region. A broken vertical line represents the composition of a hydrate. Since the solubility of lithium chlorate in water was not determined at temperatures above 98.9° C., the part of the solubility curve representing α-lithium chlorate in equilibrium with solution from 98.9° C. to 127.5° has been drawn in as a broken line.

TABLE I

THE SYSTEM $LiClO_3$–H_2O

	Wt. % $LiClO_3$	Wt. % H_2O	Method	Temperature (° C.)	Nature of the solid phases
1	—	100.0	Thermal analysis	0.0	Ice
2	10.4	89.6	"	− 6.5	"
3	20.0	80.0	"	−14.2	"
4	29.2	70.8	"	−26.2	"
5	30.2	69.8	"	−28.6	"
6	36.0	64.0	"	−40.4	"
7	37.3	62.7	"	−43.3	Ice–$LiClO_3.3H_2O$ (eutectic)
8	45.8	54.2	Solubility	−16.9	$LiClO_3.3H_2O$
9	52.8	47.2	"	− 1.5	"
10	56.7	43.3	"	3.0	"
11	57.9	42.1	"	5.2	"
12	58.7	41.3	"	6.0	"
13	60.8	39.2	"	8.1	"
14	68.1	31.9	"	6.0	"
15	70.8	29.2	"	3.0	"
16	73.1	26.9	Thermal analysis	− 0.1	$LiClO_3.3H_2O$–$LiClO_3.H_2O$ (eutectic)
17	73.6	26.4	Solubility	3.0	$LiClO_3.H_2O$
18	74.2	25.8	"	5.6	"
19	74.1	25.9	"	6.0	"
20	75.1	24.9	"	8.5	"
21	75.7	24.3	"	10.5	"
22	77.5	22.5	"	14.0	"
23	78.0	22.0	"	15.0	"
24	78.5	21.5	"	16.0	"
25	79.3	20.7	"	18.0	"
26	81.9	18.1	"	20.5	$LiClO_3.H_2O$–$(LiClO_3)_4.H_2O$ (peritectic)

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TABLE I (*concluded*)

	Wt. % $LiClO_3$	Wt. % H_2O	Method	Temperature (° C.)	Nature of the solid phases
27	82.0	18.0	Solubility	21.5	$(LiClO_3)_4.H_2O$
28	82.6	17.4	"	25.0	"
29	83.4	16.6	"	30.2	"
30	83.6	16.4	"	32.6	"
31	85.2	14.8	"	38.5	"
32	78.7	21.3	Thermal analysis	−10.5	$LiClO_3.3H_2O$–$(LiClO_3)_4.H_2O$ (eutectic)
33	82.7	17.3	"	−25.0	$LiClO_3.3H_2O$–β-$LiClO_3$ (eutectic)
34	86.7	13.3	Solubility	44.2	β-$LiClO_3$
35	87.2	12.8	"	47.9	"
36	87.8	12.2	"	54.0	"
37	89.5	10.5	"	63.2	"
38	91.0	9.0	"	72.8	"
39	92.4	7.6	"	81.7	"
40	93.7	6.3	"	86.2	"
41	93.8	6.2	"	90.7	"
42	94.8	5.2	"	94.2	"
43	95.5	4.5	"	97.5	"
44	95.9	4.1	"	98.9	"
45	100.0	0.0	Thermal analysis	127.5	α-$LiClO_3$

Since Calvert's results for the X-ray diffraction pattern of lithium chlorate at room temperature are in agreement with ours but his are more extensive, we reproduce only Calvert's results, in Table II.

In regard to the dilatometer results, it is sufficient to say that the $\beta \rightarrow \alpha$ transformation took place at 108° and at 106° in two successive cycles with rising temperature, and that the reverse change, $\alpha \rightarrow \beta$, took place at 80° C. and 84.1° C.

The results of the thermal analysis of the anhydrous salt are contained in Table III.

The System Lithium Chlorate – Lithium Chloride – Water

It was found that the time of stirring required for the attainment of equilibrium varies considerably, depending on the nature of the equilibrium solid phase or phases. Because of this uncertainty, equilibrium was always approached from two directions. A mixture of appropriate composition was divided into equal parts and treated as follows. One part was heated until all the solid phase had passed into solution, whereas the other was frozen until all the solution had solidified. These two portions were then stirred in tubes in the thermostat until the compositions of the liquid phases in each portion had become identical. For solutions containing up to 10% lithium chloride, the equilibrium stirring time was found to be from two to three days. When the solutions were more concentrated in lithium chloride, and particularly when the solid phase was the monohydrate or dihydrate of lithium chloride, five or six days were necessary for the attainment of equilibrium.

Solubility isotherms were determined at 3.0°, 6.0°, 8.5°, and 25.0° C., employing the Schreinemakers' method of "wet residues" for the determination of the nature of the equilibrium solid phase.

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TABLE II

X-RAY DIFFRACTION PATTERN OF β-$LiClO_3$ (CALVERT) AT ROOM TEMPERATURE

d (kX)	I	d (kX)	I
3.91	9.5	1.441	4.0
3.79	10.0	1.428	0.4
3.42	9.0	1.416	0.5
2.81	10.0	1.378	1.0
2.71	8.0	1.337	1.4
2.39	3.0	1.331	1.7
2.26	3.4	1.322	0.7
2.13	2.7	1.295	3.0
2.05	0.9	1.255	0.9
1.947	1.1	1.236	1.1
1.879	1.3	1.223	1.0
1.795	0.9	1.213	1.0
1.726	1.1	1.188	1.0
1.665	3.2	1.153	0.9
1.629	1.3	1.140	0.4
1.576	0.9	1.128	0.6
1.549	1.1	1.119	0.8
1.539	1.0	1.078	0.7
1.510	1.1	1.064	0.6
1.500	2.0	1.060	0.9
1.469	0.9	1.040	0.9
1.027	3.5	0.836	1.1
1.025	2.6	0.834	1.0
0.993	1.1	0.831	2.5
0.991	0.9	0.829	2.0
0.985	0.5	0.824	2.1
0.975	0.5	0.822	1.1
0.972	0.5	0.818	1.4
0.969	0.5	0.816	0.4
0.967	0.5	0.812	0.4
0.954	1.6	0.807	0.2
0.933	1.2	0.805	1.7
0.931	1.0	0.803	1.5
0.926	0.2	0.801	1.4
0.923	0.3	0.794	1.6
0.920	0.2	0.792	1.4
0.901	0.8	0.788	1.4
0.898	0.7	0.787	0.6
0.888	0.6	0.784	0.6
0.847	1.0	0.782	2.0
0.844	0.9	0.780	0.5
0.841	0.8	0.774	2.6
0.839	0.6		

TABLE III

THERMAL ANALYSIS OF ANHYDROUS SALT

Rising temperature		Falling temperature	
Transformation	Temperature (° C.)	Transformation	Temperature (° C.)
$\alpha \rightarrow$ Melt	127.4–127.5	Melt $\rightarrow \alpha$	127.4–127.5
$\beta \rightarrow \alpha$	106.1	$\alpha \rightarrow \beta$	98.2
$\beta \rightarrow \alpha$	103.6	$\alpha \rightarrow \beta$	99.8

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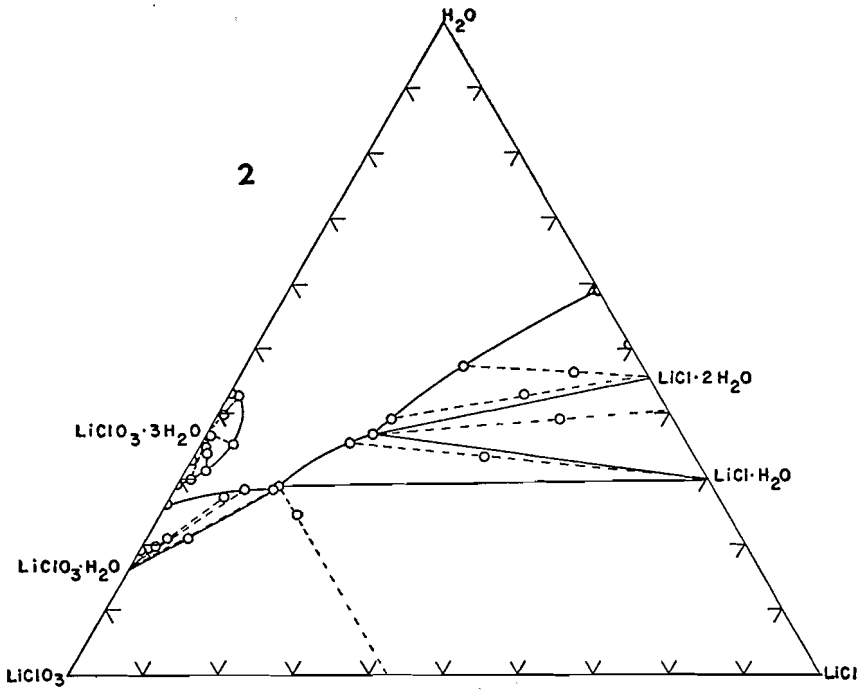

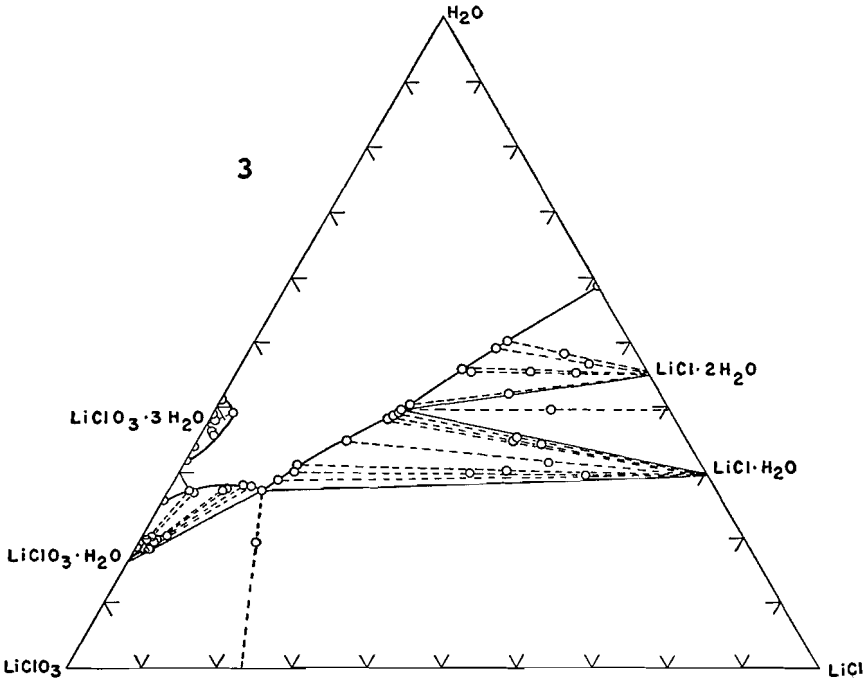

FIG. 2. System $LiClO_3$–$LiCl$–H_2O at 3.0° C.
FIG. 3. System $LiClO_3$–$LiCl$–H_2O at 6.0° C.

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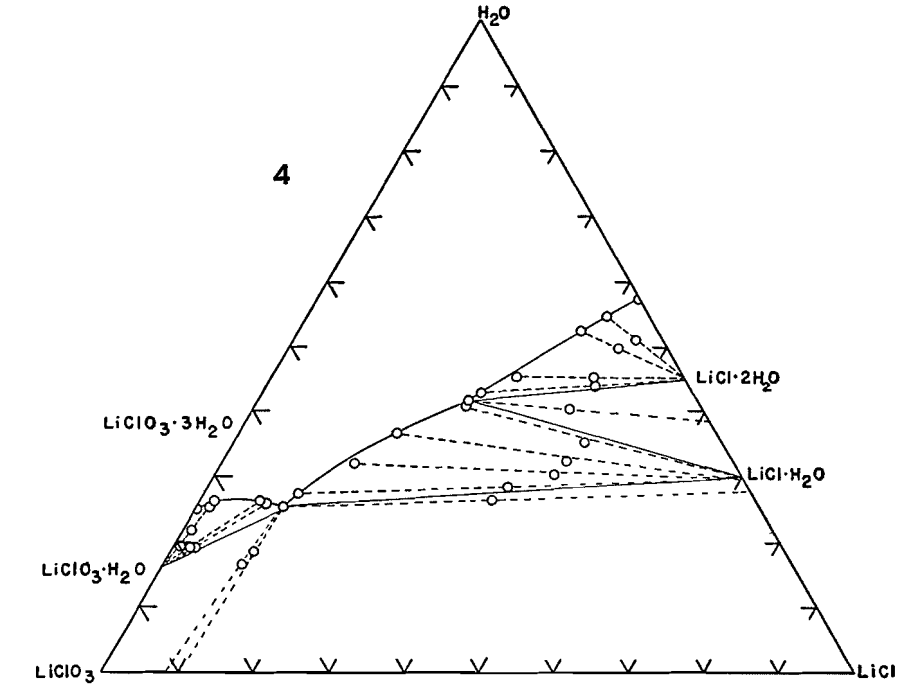

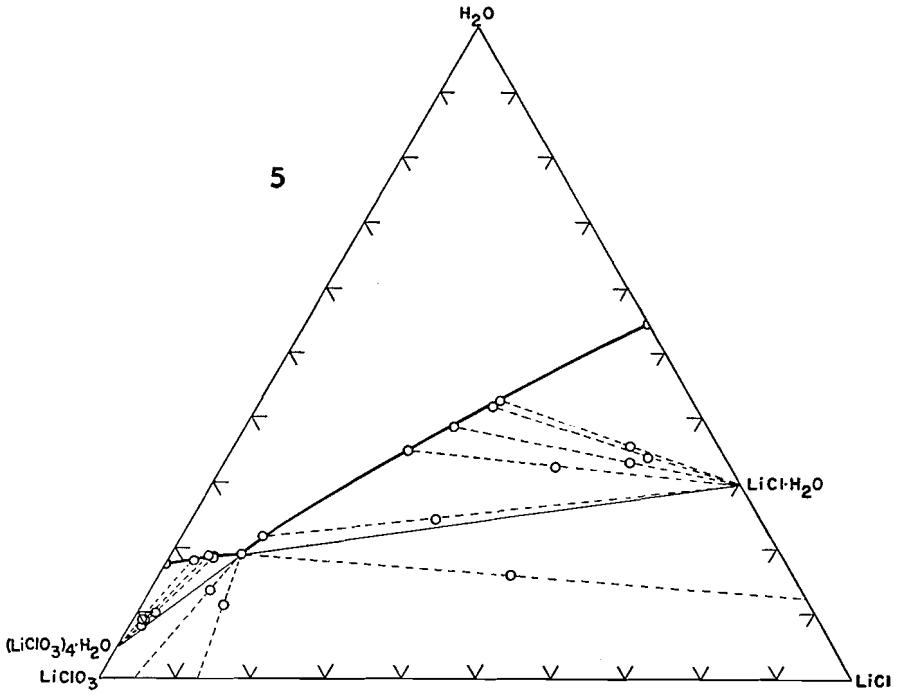

FIG. 4. System $LiClO_3$–LiCl–H_2O at 8.5° C.
FIG. 5. System $LiClO_3$–LiCl–H_2O at 25.0° C.

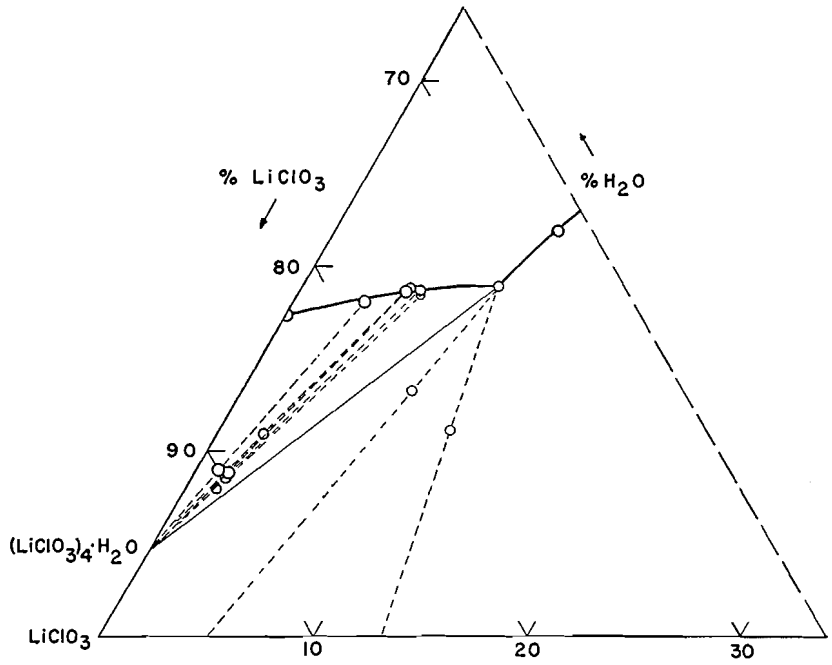

FIG. 6. Enlarged portion of Fig. 5.

The data for the isothermal ternary studies are given in Tables IV, V, VI, and VII and they are reproduced graphically in Figs. 2, 3, 4, and 5, respectively. Fig. 6 is an enlargement of the lithium chlorate corner of the 25.0° isotherm.

As will be seen later, we believe that the peculiar hydrate which is claimed by Berg (1) to have the formula $(LiClO_3)_3.H_2O$, and which is thought by Kraus and Burgess (5) to be an anhydrous γ form, really has the formula $(LiClO_3)_4.H_2O$. As additional evidence of this, a sample of the wet residue from Expt. 7, Table V, was submitted to microscopic examination. Comparison of these crystals with the photomicrographs of Berg, left no doubt that they represent the same solid phase. A photomicrograph of one of these crystals is reproduced as Fig. 7.

Since, in the ternary system, the stable hydrate of lithium chloride was the dihydrate at temperatures up to and including 8.5° C. and that stable at 25° was the monohydrate, we determined the transition temperature of the reaction

$$LiCl.2H_2O \leftrightarrow LiCl.H_2O + H_2O$$

by thermal analysis. We found this temperature to be 12.5°±0.1° C., in agreement with the value of 12.5°, found by Hüttig and Reuscher (3).

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PLATE I

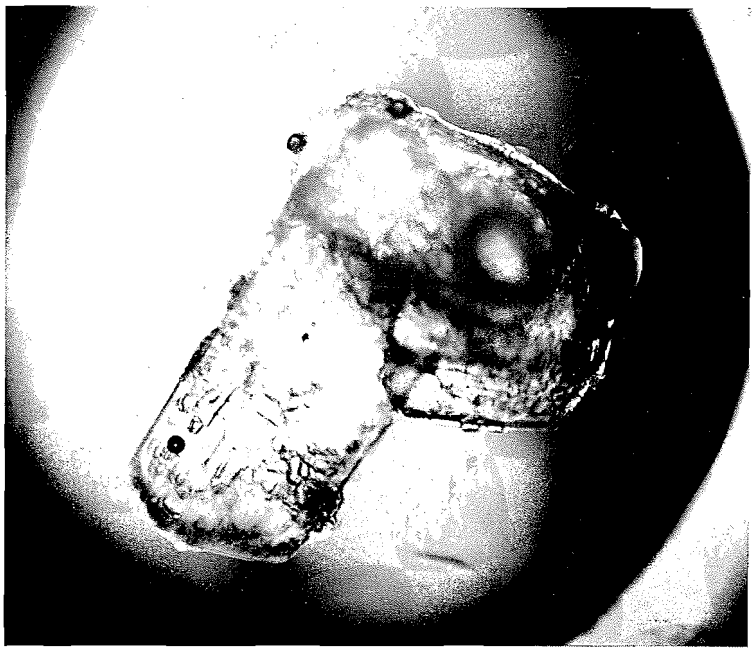

FIG. 7.

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RESULTS

TABLE IV

ISOTHERM FOR 3.0±0.05° C.

	Solution		Wet residue		
	Wt. % $LiClO_3$	Wt. % LiCl	Wt. % $LiClO_3$	Wt. % LiCl	Nature of the solid phase
1	56.7	—	—	—	$LiClO_3.3H_2O$
2	55.8	1.3	59.4	0.9	"
3	62.2	4.3	62.7	0.7	"
4	66.0	2.8	64.5	1.6	"
5	68.7	1.5	64.1	0.8	"
6	70.8	—	67.0	—	"
7	73.6	—	80.7	—	$LiClO_3.H_2O$
8	65.6	7.1	78.4	1.9	"
9	62.4	9.4	76.2	3.8	"
10	58.5	13.1	73.6	5.6	"
11	57.5	13.7	57.1	18.1	$LiClO_3.H_2O + LiCl.H_2O$
12	44.7	19.9	27.9	38.8	$LiCl.H_2O$
13	40.9	22.1	15.0	46.0	$LiCl.H_2O + LiCl.2H_2O$
14	37.4	23.5	17.8	39.3	$LiCl.2H_2O$
15	23.9	29.1	9.6	44.2	"
16	—	41.0	—	49.3	"

TABLE V

ISOTHERM FOR 6.0±0.05° C.

	Solution		Wet residue		
	Wt. % $LiClO_3$	Wt. % LiCl	Wt. % $LiClO_3$	Wt. % LiCl	Nature of the solid phases
1	58.7	—	61.1	—	$LiClO_3.3H_2O$
2	58.3	2.5	61.3	0.8	"
3	62.7	1.8	62.7	1.0	"
4	68.1	—	66.1	—	"
5	74.1	—	81.4	—	$LiClO_3.H_2O$
6	70.0	2.7	79.5	0.9	"
7	69.7	3.4	78.6	1.2	"
8	65.8	7.1	79.9	1.9	"
9	64.9	7.5	78.8	2.0	"
10	62.6	9.6	76.5	3.1	"
11	61.4	10.7	78.0	2.2	"
12	60.4	12.3	65.1	15.6	$LiClO_3.H_2O + LiCl.H_2O$
13	57.5	13.7	16.0	54.3	$LiCl.H_2O$
14	54.8	15.2	31.4	38.9	"
15	53.9	15.0	26.2	43.5	"
16	45.2	20.0	20.0	48.2	"
17	38.2	23.7	23.2	42.0	"
18	37.2	24.0	19.7	46.0	"
19	36.2	24.6	22.2	42.3	$LiCl.H_2O + LiCl.2H_2O$
20	35.7	24.9	16.6	44.8	$LiCl.2H_2O$
21	34.1	25.4	20.0	37.8	"
22	24.4	29.7	15.5	39.0	"
23	23.5	30.0	9.7	45.1	"
24	18.3	32.5	7.1	46.0	"
25	16.3	33.5	7.1	42.0	"
26	—	41.1	—	49.5	"

TABLE VI

ISOTHERM FOR 8.5±0.05° C.

	Solution		Wet residue		
	Wt. % $LiClO_3$	Wt. % LiCl	Wt. % $LiClO_3$	Wt. % LiCl	Nature of the solid phases
1	75.0	—	—	—	$LiClO_3.H_2O$
2	73.4	1.5	77.5	0.9	"
3	72.0	1.9	80.0	0.8	"
4	66.1	7.7	79.0	2.0	"
5	65.6	8.8	78.3	2.5	"
6	64.2	11.2	70.7	11.9	$LiClO_3.H_2O + LiCl.H_2O$
7	63.5	11.2	73.3	11.2	"
8	62.7	11.6	35.1	38.4	"
9	60.5	12.3	31.9	39.7	$LiCl.H_2O$
10	50.8	17.4	24.9	44.9	"
11	31.3	27.7	18.3	46.3	"
12	30.6	27.8	17.8	41.9	$LiCl.H_2O + LiCl.2H_2O$
13	28.2	28.9	12.8	43.4	$LiCl.2H_2O$
14	22.5	32.2	12.2	42.7	"
15	10.4	37.3	6.7	43.7	"
16	5.6	39.7	3.8	45.3	"
17	—	42.7	—	50.3	"

TABLE VII

ISOTHERM FOR 25.0±0.05° C.

	Solution		Wet residue		
	Wt. % $LiClO_3$	Wt. % LiCl	Wt. % $LiClO_3$	Wt. % LiCl	Nature of the solid phases
1	82.6	—	—	—	$(LiClO_3)_4.H_2O$
2	78.7	3.3	90.0	1.0	"
3	76.4	5.0	89.6	1.6	"
4	76.1	5.1	86.9	2.1	"
5	75.7	5.6	89.9	1.5	"
6	75.8	5.7	87.8	2.3	"
7	75.9	5.8	90.7	1.4	"
8	72.3	9.2	78.8	8.0	$(LiClO_3)_4.H_2O + LiCl.H_2O$
9	71.8	9.2	78.1	10.8	"
10	71.6	9.2	37.5	46.7	"
11	67.7	10.7	43.1	32.4	$LiCl.H_2O$
12	41.7	23.3	23.2	44.4	"
13	33.8	27.7	13.0	53.8	"
14	27.0	31.3	10.1	55.7	"
15	25.5	31.7	11.7	52.5	"
16	—	45.5	—	—	"

DISCUSSION OF RESULTS

Apart from a few slight refinements in temperature and composition, the solubility curves in the binary equilibrium diagram, Fig. 1, are essentially the same as those previously obtained by Kraus and Burgess (5) and by Berg (1). In general, the results of previous workers indicate a lower solubility than do our results.

The trihydrate of lithium chlorate melts congruently but the equilibrium curve is very flat and this makes it difficult to read off the exact melting

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temperature from the curve. Neither was an attempt to determine the melting point by direct experiment successful, since it is difficult to prepare and maintain the mixture having the exact composition of the trihydrate. We found, experimentally, that the trihydrate exists at 8.1°, while reference to Fig. 4, the 8.5° isotherm, shows that trihydrate is absent. The flat maximum on the equilibrium curve, as well as we could read it, appeared to us to lie at 8.4° C. Kraus and Burgess (5) reported 8.0° and Berg (1) from 8.1 to 8.3°.

The trihydrate participates in four eutectics, two stable ones at −43.3° and −0.1° C. respectively, and two metastable at −10.5° and −25° respectively. The other solid phases at the eutectics are listed in Table I.

The solubility curves of the binary system indicate that two different solid phases are in equilibrium with solution in the temperature ranges −0.1° to 20.5° C. and 20.5° to 42.0°, respectively. The ternary isotherms for 3.0°, 6.0°, 8.5°, and 25.0° show clearly what the phases are. In the lower temperature range, the solid phase is the monohydrate of lithium chlorate, as claimed by Kraus and Burgess and by Berg.

The isothermal ternary study at 25.0° proved to be the most instructive, since it has refuted the claims both of Kraus and Burgess and of Berg. Fig. 6, which is an enlargement of the lithium chlorate corner of the 25° isotherm, shows tie lines running consistently into a composition corresponding to the hydrate $(LiClO_3)_4.H_2O$. Since the existence or non-existence of this hydrate is important, it is well to say a few words about the attainable experimental accuracy in this region. The successful application of the Schreinemakers' method of "wet residues" depends on the accuracy of the chemical analyses employed and on the extent to which mother liquor is removed from the "wet" solid phase. At 25°, we never found more than 11% water in this solid phase; this could hardly be improved upon, since the dry hydrate itself contains 4.7% water. Although the inaccuracy of our chlorate determinations may amount to 0.4%, our gravimetric determinations of chloride were much better than this. In Fig. 6, the tie lines joining the compositions of the liquid phase and the wet residue cross the lithium chlorate reference lines at an angle of about 70°. Hence, if there is an error of 0.4% in the lithium chlorate determination this would lead to an error of about 0.2% lithium chlorate in the composition of the equilibrium solid phase. The consequences of an error in the lithium chloride analysis are far more serious, because the directions of the tie lines and the reference line of lithium chloride approach one another. The fact that none of the tie lines ever crossed, and that they all converged to a single composition when extrapolated, indicates that the analyses were of sufficient accuracy and that equilibrium had been reached in all cases. As a check on the possibility of any consistent error in the procedure, the data were compared with a point which had been determined a month previously. The points all indicated the same solid phase and therefore left no doubt that the hydrate stable at 25° C. has the composition corresponding to the formula $(LiClO_3)_4.H_2O$.

In Fig. 6 there are no experimentally determined solubilities representing solutions containing from 5.8 to 9.16% lithium chloride. In order to prove that

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a break did not occur in the solubility curve in this range, the wet residues from the two determinations 7 and 8 were investigated under the polarizing microscope. The solid phase was the same in both cases, although a slight amount of the monohydrate of lithium chloride was present in number 8. Therefore, the invariant solutions 8, 9, and 10 were actually in equilibrium with the one-fourth hydrate of lithium chlorate and the monohydrate of lithium chloride.

The hydrate which Berg claims contains one-third of a mole of water we think contains only one-fourth of a mole of water, but we are referring to the same hydrate. We convinced ourselves of this by comparing our photomicrograph of wet residue 7 with those obtained by Berg of his supposed one-third hydrate. If, therefore, our hydrate contains one-fourth of a mole of water, so does Berg's. Berg deduced the composition of his hydrate by the method of the peritectic halt time and this is far from being a sensitive method. Kraus and Burgess, on the other hand, thought they had eliminated Berg's claim for a hydrate of low water content on the ground that a mixture containing 6.55% water definitely showed the presence of solution between 21.0° and 41.5° C. If the solid were really the one-third hydrate, which contains 6.2% water, the mixture would not form an observable amount of solution. If, however, the hydrate contains only one-fourth of a mole of water, as we claim, about one-third of the above mixture would liquefy.

At 42.0° C., the one-fourth hydrate undergoes a peritectic transition to anhydrous salt and solution. The modification of anhydrous salt formed at 42° C. is the first (low temperature) modification of two allotropic forms. This form is the one stable at room temperature and corresponds to the β form of Kraus and Burgess. Of the three methods used to investigate the transition from β to α, viz. thermal analysis, dilatometry, and X-ray diffraction, only the former method gave a really satisfactory result and it indicated that the transition temperature was 99.8° C. This value compares favorably with the values obtained by Kraus and Burgess and by Berg. The dilatometer showed a marked increase in volume, accompanying the β to α transition. We have applied the techniques of dilatometry, thermal analysis, solubility, and X-ray diffraction in an attempt to find the supposed β to γ transition, but always without result. The heating and cooling curves of anhydrous salt showed no break and the expansion and contraction of the dilatometer was perfectly regular. Finally, an X-ray diffraction picture was taken of a sample which had never been heated; this was then heated for a week at 80° C., allowed to cool, and immediately photographed again. The two patterns were identical.

If the hemihydrate of lithium chlorate claimed by Wächter (8), Troost (7), Potilitzin (6), and Brühl (2) did indeed exist, it would be formed from the monohydrate in a peritectic transformation. This would appear as a break in the solubility curve, in the binary system. No such break occurred between −0.1° and 20.5° C. The monohydrate is the solid phase in equilibrium with solution in this temperature interval. Neither was there any break in the solubility curve from 20.5° to 42° C. In this temperature range, the stable solid phase is the one-fourth hydrate. Therefore, there is no doubt that the

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hemihydrate of lithium chlorate does not exist as a stable phase and there have been no indications of its ever appearing as a metastable phase throughout this study.

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A STUDY OF THE REACTIONS OF AMMONIUM SULPHAMATE WITH AMIDES AND UREAS[1]

By Paul E. Gagnon, Jean L. Boivin,[2] and Catherine Haggart[3]

ABSTRACT

The preparation of nitriles from amides and ammonium sulphamate was investigated. The method was found to be generally applicable and good yields were obtained in most cases. The mechanism of the reaction involved the liberation of ammonia and the formation of ammonium N-carbonyl sulphamates, which decomposed into nitriles and ammonium bisulphate.

The mechanism for the formation of guanidine and cyanuric acid from ureas was elucidated. The effects of methyl, phenyl, acetyl, and benzoyl groups on the reactivity of the urea molecule were determined. Methylamine and aniline were obtained from methylurea and phenylurea together with guanidine and cyanuric acid. Acetylurea and benzoylurea formed acetonitrile and benzonitrile, the yield of guanidine being low but that of cyanuric acid very high.

INTRODUCTION

Amides and Ammonium Sulphamate

Nitriles had been obtained before from amides by treatment with phosphorus pentachloride, phosphorus pentoxide, phosphorus oxychloride, and thionyl chloride. Short and long chain aliphatic and aromatic amides required the use of different dehydrating agents.

In 1950 Boivin (2) reported that nitriles were formed when simple aliphatic and aromatic amides (1) were heated with ammonium sulphamate (II) at 180–190° C. The reaction proceeded with the evolution of ammonia and the formation of ammonium bisulphate.

$$\underset{\text{I}}{RCONH_2} + \underset{\text{II}}{H_2NSO_3NH_4} \rightarrow RCN + NH_4HSO_4 + NH_3$$

In order to determine whether this method of preparing nitriles was generally applicable, a series of amides, including short and long chain aliphatic, aromatic, α-substituted aliphatic, and heterocyclic amides were heated with ammonium sulphamate. The corresponding nitriles were obtained in fairly good yields. They are listed in Table I.

It was known that ammonium sulphamate did not behave as a normal dehydrating agent (3). Berglund (1) found that when heated alone at 170–180° C. it was transformed into ammonium imidodisulphonate (III) and ammonia.

$$2\ H_2NSO_3NH_4 \rightarrow \underset{\text{III}}{HN(SO_3NH_4)_2} + NH_3$$

This showed that there was the possibility of the formation of an intermediate when amides were heated with ammonium sulphamate. The possibility was

[1]*Manuscript received May 31, 1956.*
Contribution from the Department of Chemistry, Laval University, Quebec, Que., with financial assistance from the Defence Research Board of Canada. This paper constitutes part of a thesis submitted to the Graduate School, Laval University, in partial fulfillment of the requirements for the degree of Doctor of Science.
[2]*Defence Research Board, C.A.R.D.E., Valcartier, Que.*
[3]*Graduate student, holder of a National Research Council of Canada Studentship in 1955–56.*

substantiated during the present work. In fact, it was found that mixtures of amides and ammonium sulphamate when heated directly at 200° C. produced nitriles in very low yields. It was necessary to heat the mixtures initially at 150° C. and to raise the temperature slowly to 200° C. Furthermore Cuprey (4) mentioned that amides reacted with sulphamic acid to yield N-carbonyl sulphamic acids.

$$RCONH_2 + H_2NSO_3H \rightarrow RCONHSO_3H + NH_3$$

It thus seemed probable that the intermediate formed during the reaction of amides and ammonium sulphamate was of the ammonium N-carbonyl sulphamate type. In order to prove this unequivocally, seven ammonium N-carbonyl sulphamates were prepared; amides were treated with a solution of sulphuric acid in acetic anhydride and formed the amide salt of amido sulphonic acids, which with ammonium hydroxide formed ammonium N-carbonyl sulphamates.

$$2\ RCONH_2 + H_2SO_4 + (CH_3CO)_2O \rightarrow RCONHSO_3H.H_2NOCR + 2\ CH_3COOH$$
$$RCONHSO_3H.H_2NOCR + NH_4OH \rightarrow RCONHSO_3NH_4 + RCONH_2$$

When these ammonium salts were heated at 170–180° C. nitriles and ammonium bisulphate were formed.

$$RCONHSO_3NH_4 \rightarrow RCN + NH_4HSO_4$$

The yields of nitriles from ammonium N-carbonyl sulphamates were very good, varying from 90 to 95%. The results are shown in Table II.

Thus the formation of nitriles from amides and ammonium sulphamate involves a condensation of the amide with ammonium sulphamate by liberation of ammonia to yield ammonium N-carbonyl sulphamates, which decompose into nitriles and ammonium bisulphate.

$$RCONH_2 + H_2NSO_3NH_4 \rightarrow NH_3 + RCONHSO_3NH_4$$
$$RCONHSO_3NH_4 \rightarrow RCN + NH_4HSO_4$$

The mechanism indicated that secondary amides, which cannot be readily dehydrated, should produce nitriles and amines when heated with ammonium sulphamate. Three secondary amides, namely, acetanilide, *o*-acetamidobenzoic acid, and *p*-acetamidobenzoic acid were heated with ammonium sulphamate. In each case acetonitrile was isolated together with aniline, *o*-aminobenzoic acid, and *p*-aminobenzoic acid.

Ureas and Ammonium Sulphamate

Boivin and Lovecy (3) reported that guanidine was formed when urea was heated with ammonium sulphamate. It was thus of interest to determine the behavior not only of urea but also of mono- and di-substituted ureas towards ammonium sulphamate.

Urea

When urea was heated with ammonium sulphamate, guanidine and cyanuric acid were formed. The yield of guanidine varied with the temperature and time of the reaction but only slightly with the amount of ammonium sulphamate used. The results are given in Table III.

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Alkylureas

It was found that methylurea and 1,3-dimethylurea reacted with ammonium sulphamate in a manner analogous to that of urea. Methylamine was isolated from the reaction mixtures.

Methyl groups had little effect on the reactivity of the urea molecule. Guanidine was isolated and not methylguanidine. The yield of guanidine varied with the temperature and time of the reaction and the amount of ammonium sulphamate used. The results are found in Tables IV and V.

Arylureas

Monophenylurea when heated with ammonium sulphamate reacted as did the alkylureas; guanidine and cyanuric acid were formed together with aniline and diphenylurea. The yield of guanidine was affected by the amount of ammonium sulphamate used but only slightly by the temperature and time of the reaction. The results are shown in Table VI.

Diphenylurea produced only aniline and no guanidine nor cyanuric acid when heated with ammonium sulphamate.

Alkoyl and Aroylureas

The effects of alkoyl and aroyl groups on the reactivity of the urea molecule were studied. It was noted that the carbonyl of an acetyl or benzoyl group was more reactive than the carbonyl group of urea. In the reactions of acetylurea and benzoylurea with ammonium sulphamate, the substituted urea decomposed to form acetamide or benzamide and hence the corresponding nitriles and cyanuric acid. The yield of guanidine was low while that of cyanuric acid was very high. The results are listed in Tables VII and VIII.

Diacetylurea when heated with ammonium sulphamate produced only acetonitrile and no guanidine nor cyanuric acid.

Salts of Carbamylsulphamate

Boivin and Lovecy (3) reported that ammonium carbamylsulphamate was formed when urea reacted with ammonium sulphamate at 140° C.

Ammonium carbamylsulphamate was prepared in a manner analogous to the preparation of ammonium N-carbonyl sulphamates previously mentioned. Urea reacted with sulphuric acid in acetic anhydride to form urea carbamylsulphamate. This viscous salt, which could not be induced to crystallize immediately, was treated with ammonium hydroxide to form ammonium carbamylsulphamate.

$$2\ H_2NCONH_2 + H_2SO_4 + (CH_3CO)_2O \rightarrow H_2NCONHSO_3H.H_2NCONH_2 + 2CH_3COOH$$
$$H_2NCONHSO_3H.H_2NCONH_2 + NH_4OH \rightarrow H_2NCONHSO_3NH_4 + H_2NCONH_2$$

When ammonium carbamylsulphamate was heated alone, guanidine and cyanuric acid were formed. The yield of guanidine was increased by the addition of ammonium sulphamate. The results are given in Table IX.

By analogy with the reactions of amides and ammonium sulphamate, or of the intermediate ammonium N-carbonyl sulphamates, it seemed that ammonium carbamylsulphamate should produce the corresponding nitrile, which

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is cyanamide. It is well known that cyanamide in the presence of an ammonium salt is converted into guanidine or its trimer, melamine. Thus the formation of guanidine from ammonium carbamylsulphamate would proceed as follows.

$$H_2NCONHSO_3NH_4 \rightleftharpoons NH_4OCN + NH_4HSO_4$$
$$NH_4OCN \rightarrow HOCN + NH_3$$
$$3\ HOCN \rightleftharpoons (HOCN)_3$$
$$H_2NCONHSO_3NH_4 \rightarrow H_2NCN + NH_4HSO_4 + NH_3 \rightarrow H_2NC(NH)NH_3SO_4NH_4$$

In order to prove that the formation of guanidine does occur through the condensation of cyanic acid with ammonium sulphamate to form ammonium carbamylsulphamate, potassium, sodium, and urea carbamylsulphamates were heated alone and with ammonium sulphamate.

As expected, only cyanuric acid was isolated when these three salts were heated alone. It was necessary to heat the salts with ammonium sulphamate in order that guanidine be formed.

In view of the experimental results obtained the mechanism of the formation of guanidine occurs through the condensation of cyanic acid with ammonium sulphamate, forming ammonium carbamylsulphamate, which is converted into guanidine.

$$HOCN + H_2NSO_3NH_4 \rightarrow H_2NCONHSO_3NH_4 + NH_3 \rightarrow H_2NC(NH)NH_3SO_4NH_4$$

Salts of N-Methylcarbamylsulphamate

In order to determine why no methylguanidine was formed when methylurea and dimethylurea were heated with ammonium sulphamate, the behavior of ammonium N-methylcarbamylsulphamate was studied.

This salt heated alone produced only cyanuric acid. With ammonium sulphamate at temperatures not exceeding 230° C. methylguanidine together with traces of guanidine was isolated. At temperatures above 230° C. only guanidine and no methylguanidine was formed. The results are listed in Table X.

The fact that methylguanidine was readily formed from ammonium sulphamate and ammonium N-methylcarbamylsulphamate proves that the formation of this salt is an essential step in the production of methylguanidine from methylurea and dimethylurea. However, since methylguanidine is not isolated from the reactions of methylurea and dimethylurea, the formation of ammonium N-methylcarbamylsulphamate was prevented. The experimental conditions used favored the formation of ammonium carbamylsulphamate and hence guanidine.

Thus two opposing reactions were involved when methylurea or dimethylurea was heated with ammonium sulphamate; guanidine was formed in preference to methylguanidine.

From the study it is concluded that the formation of nitriles by the reaction of amides and ammonium sulphamate involves a condensation of the amide with ammonium sulphamate, the liberation of ammonia, and the formation of ammonium N-carbonyl sulphamates, which decompose into nitriles and ammonium bisulphate. This method of preparing nitriles is generally applicable to most amides.

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The formation of guanidine from urea and substituted ureas is due to the condensation of cyanic acid with ammonium sulphamate resulting in the formation of ammonium carbamylsulphamate, which is converted into guanidine and ammonium bisulphate. Alkyl and aryl ureas produce amines and alkoyl and aroyl ureas produce nitriles in addition to guanidine and cyanuric acid.

EXPERIMENTAL

Direct Synthesis of Nitriles

In a distilling flask equipped with a short column was placed ammonium sulphamate (17.10 gm., 0.15 mole) and an amide (0.1 mole). The mixture was heated in a metal bath, the temperature of which was slowly raised from 150° C. up to 190–200° C. The liquid nitriles were collected by distillation and the solid ones by vacuum distillation or extraction with a suitable solvent. The results are shown in Table I.

TABLE I

AMIDES AND NITRILES

Amides	Nitriles	M.p., °C.	B.p., °C.	Yield, %	Calc., % N	Found, % N
X	CH_3CN		81–82	10	34.15	34.20
$C_3H_7CONH_2$	C_3H_7CN		216	65	20.3	20.38
$C_4H_9CONH_2$	C_4H_9CN		142	70	16.75	16.80
$C_4H_9CONH_2$	C_4H_9CN		129–130	80	16.75	16.81
$C_5H_{11}CONH_2$	$C_5H_{11}CN$		162	80	14.43	14.38
$C_{17}H_{35}CONH_2$	$C_{17}H_{35}CN$	41.5		92	5.28	5.30
$C_4H_8(CONH_2)_2$	$C_4H_8(CN)_2$		153/6 mm.	45	25.92	25.98
o-$CH_3C_6H_4CONH_2$	*o*-$CH_3C_6H_4CN$		201–202	75	11.96	12.0
p-$CH_3C_6H_4CONH_2$	*p*-$CH_3C_6H_4CN$	30	215–216	90	11.96	11.99
$HOC_6H_4CONH_2$	HOC_6H_4CN	98		25	11.76	11.83
$C_6H_5CH_2CONH_2$	$C_6H_5CH_2CN$		206/107 mm.	45	11.96	11.94
$C_2H_5CH(C_6H_5)CONH_2$	$C_2H_5CH(C_6H_5)CN$		107/7 mm.	80	9.65	9.7
$C_6H_5OCH_2CONH_2$	$C_6H_5OCH_2CN$		115/11 mm.	65	10.52	10.58
$C_{10}H_7CH_2CONH_2$	$C_{10}H_7CH_2CN$	33	178/12 mm.	58	8.38	8.40
$C_4H_3OCONH_2$	C_4H_3OCN		148–150	15	15.05	15.09
$C_5H_3NCONH_2$	C_5H_3NCN	51		85	26.92	26.99

X = $CH_3CONHC_6H_5$ *or* *o*-$CH_3CONHC_6H_4COOH$ *or* *p*-$CH_3CONHC_6H_4COOH$.

Preparation of Nitriles from Ammonium N-Carbonyl Sulphamates

An amide (0.1 mole) was added to cold mixture of acetic anhydride (250 ml.) and sulphuric acid (49.0 gm., 0.5 mole). The solution was cooled to −20° C. in an acetone – dry-ice bath. The bulky white solid which separated out was filtered, washed well with anhydrous ethyl ether, and dissolved in ethanol (250 ml.). The alcoholic solution was treated with ammonium hydroxide (80 ml.) and cooled. The ammonium N-carbonyl sulphamates were isolated as crystalline solids which are not described in the literature. The results are shown in Table II.

Upon the heating of these ammonium salts at 170–180° C. nitriles and ammonium bisulphate were isolated. The nitriles isolated from ammonium N-carbonyl sulphamates are given in Table II.

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Ureas and Ammonium Sulphamate

The ureas (0.1 mole) and ammonium sulphamate (0.1, 0.2, 0.3 mole) were heated in the same manner as described for the amides and ammonium sulphamate. The temperature and time of the reaction were varied.

The reaction products were water leached and the filtrates were analyzed for guanidine and cyanuric acid. Guanidine was estimated as the picrate and cyanuric acid as melamine cyanurate. The results are listed in Tables III, IV, V, VI, VII, and VIII.

TABLE II

AMMONIUM N-CARBONYL SULPHAMATES AND NITRILES

Ammonium N-carbonyl sulphamates	M.p., °C.	Yield, %	Calc.		Found		Nitriles	Yield, %
			% N	% SO_3	% N	% SO_3		
$C_{17}H_{35}CONHSO_3NH_4$	115	90	7.37	21.05	7.39	20.98	$C_{17}H_{35}CN$	95
$C_4H_8(CONHSO_3NH_4)_2$	208	85	16.56	47.33	16.48	47.5	$C_4H_8(CN)_2$	90
$C_7H_7CONHSO_3NH_4$	140	95	12.07	34.49	12.0	34.53	C_7H_7CN	97
$C_7H_7CONHSO_3NH_4$	160	75	12.07	34.49	11.99	34.51	C_7H_7CN	95
$HOC_6H_4CONHSO_3NH_4$	143	80	11.96	34.19	11.91	34.1	HOC_6H_4CN	95
$C_6H_5CH_2CONHSO_3NH_4$	127	95	12.07	34.48	11.99	34.51	$C_6H_5CH_2CN$	85
$C_{10}H_7CH_2CONHSO_3NH_4$	157	85	9.93	28.39	9.97	28.43	$C_{10}H_7CH_2CN$	95

TABLE III

UREA AND AMMONIUM SULPHAMATE

Molar ratio H_2NCONH_2: $H_2NSO_3NH_4$	Temp., °C.	Time in minutes		Yield, %	
		Total	Above 200° C.	Guanidine	Cyanuric acid
1:1	200	50	45	30.1	32.1
1:1	230	75	70	30.2	3.0
1:2	200	50	45	33.9	2.0
1:2	200	74	70	33.8	4.6
1:2	230	23	15	59.2	14.0
1:2	230	14	8	59.2	4.0
1:2	250	14	5	40.7	16.0
1:2	275	8	4	40.3	14.0
1:3	200	50	45	32.4	1.0
1:3	230	75	70	35.8	4.0

TABLE IV

METHYLUREA AND AMMONIUM SULPHAMATE

Molar ratio $CH_3NHCONH_2$: $H_2NSO_3NH_4$	Temp., °C.	Time in minutes		Yield, %	
		Total	Above 200° C.	Guanidine	Cyanuric acid
1:1	250	20	10	Nil	25.6
1:2	200	65	59	8.5	Traces
1:2	210	61	48	25.4	2.3
1:2	220	45	31	27.1	4.2
1:2	230	30	13	27.1	4.2
1:2	250	14	4	28.8	4.9
1:3	250	20	10	32.2	7.0
1:3	250	30	20	49.4	4.2

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TABLE V

DIMETHYLUREA AND AMMONIUM SULPHAMATE

Molar ratio $CH_3NHCONHCH_3$: $H_2NSO_3NH_4$	Temp., ° C.	Time in minutes		Yield, %	
		Total	Above 200° C.	Guanidine	Cyanuric acid
1:1	250	16	10	2.0	2.3
1:1	250	28	20	2.0	Traces
1:2	200	110	100	1.8	Traces
1:2	220	48	38	2.0	Traces
1:2	230	25	16	11.0	Traces
1:2	230	42	35	25.0	Traces
1:2	250	23	10	29.0	Traces
1:2	250	31	20	29.0	Traces
1:3	250	16	10	35.7	2.3
1:3	250	28	20	35.7	2.3

TABLE VI

MONOPHENYLUREA AND AMMONIUM SULPHAMATE

Molar ratio $C_6H_5NHCONH_2$: $H_2NSO_3NH_4$	Temp., ° C.	Time in minutes		Yield, %	
		Total	Above 200° C.	Guanidine	Cyanuric acid
1:1	230	35	20	12.5	17.0
1:2	200	180	170	Nil	Nil
1:2	230	70	60	24.0	26.0
1:2	250	23	14	24.0	26.0
1:2	275	18	4	25.0	26.5
1:3	250	25	14	30.0	15.0
1:3	275	18	4	50.0	7.0

TABLE VII

MONOACETYLUREA AND AMMONIUM SULPHAMATE

Molar ratio $CH_3CONHCONH_2$: $H_2NSO_3NH_4$	Temp., ° C.	Time in minutes		Yield, %	
		Total	Above 200° C.	Guanidine	Cyanuric acid*
1:1	230	60	25	13.0	85.0
1:2	200	120	105	23.7	75.0
1:2	230	60	25	25.1	81.0
1:2	230	75	50	25.4	79.0
1:2	250	30	10	25.1	81.0
1:2	275	45	4	17.0	50.0
1:3	230	60	25	26.2	76.0

**The method of determining cyanuric acid by the use of melamine is known to give high results.*

Salts of Carbamylsulphamate

The viscous urea salt was prepared as described by Boivin and Lovecy (3). After decanting, the salt was well washed with anhydrous ethyl ether, dissolved in ethanol (50 ml.), and anhydrous ethyl ether was added (300 ml.). The mixture was left standing overnight at room temperature. The white needle-like solid was filtered, well washed with ether, and dried *in vacuo* for two days. Pure urea carbamylsulphamate was obtained, m.p. 123° C. Yield, 30%.

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TABLE VIII

MONOBENZOYLUREA AND AMMONIUM SULPHAMATE

Molar ratio $C_6H_5CONHCONH_2$: $H_2NSO_3NH_4$	Temp., ° C.	Time in minutes		Yield, %	
		Total	Above 200° C.	Guanidine	Cyanuric acid*
1:1	230	45	40	10.0	88.0
1:2	200	150	130	23.0	70.0
1:2	230	50	45	27.0	80.0
1:2	230	45	30	25.0	80.0
1:2	275	18	3	26.0	80.0
1:3	230	45	40	27.0	78.0

**The method of determining cyanuric acid by the use of melamine is known to give high results.*

Calculated for $C_2H_7O_5N_4S$: C, 12.06%; H, 3.52%; N, 28.14%; S, 16.08%. Found: C, 12.01%; H, 3.5%; N, 28.2%; S, 16.2%.

The ammonium, sodium, and potassium urea carbamylsulphamates were prepared by treating an alcoholic solution of the viscous urea salt with an aqueous solution of the appropriate hydroxide. Ammonium carbamylsulphamate was isolated, m.p. 167–168° C. (reported m.p. 167.5–168° C.). Sodium carbamylsulphamate had no definite melting point but decomposed at 220° C. Yield, 70%. Calculated for $CH_3O_4N_2S$ Na: N, 17.28%; SO_3, 49.38%. Found: N, 17.32%; SO_3, 49.41%. Potassium carbamylsulphamate had no definite melting point but decomposed at 200° C. Yield, 75%. Calculated for $CH_3O_4N_2SK$: N, 15.73%; SO_3, 44.90%. Found: N, 15.78%; SO_3, 44.80%.

The carbamylsulphamates were heated alone and with ammonium sulphamate in the same manner as described for the reactions of amides and ammonium sulphamate. The reaction products were water leached and the filtrates were analyzed for guanidine and cyanuric acid. The results obtained for ammonium carbamylsulphamate are listed in Table IX.

TABLE IX

AMMONIUM CARBAMYLSULPHAMATE

Molar ratio $H_2NCONHSO_3NH_4$: $H_2NSO_3NH_4$	Temp., ° C.	Time in minutes		Yield, %	
		Total	Above 200° C.	Guanidine	Cyanuric acid
1:0	200	25	20	Nil	50.0
1:0	230	25	20	19.0	70.0
1:0	250	18	10	35.0	35.0
1:1	200	27	20	16.0	25.0
1:1	230	18	10	49.0	11.0
1:2	230	25	20	69.0	14.0
1:2	250	25	20	97.0	2.0
1:4	230	16	10	76.0	7.0
1:4	230	28	20	80.0	7.0

Salts of N-Methylcarbamylsulphamate

Methylurea (73.0 gm., 1.0 mole) was added to a cold mixture of acetic anhydride (250 ml.) and sulphuric acid (49.0 gm., 0.5 mole). The solution

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was cooled to −20° C. and the viscous methylurea salt was decanted. Crystallization was effected by dissolving the salt in ethanol (150 ml.) and adding anhydrous ethyl ether (100 ml.). The white crystalline methylurea salt was isolated, m.p. 107–108° C. Yield, 80%. Calculated for $C_4H_{11}O_5N_4S$: N, 24.67%; SO_3, 35.2%. Found: N, 24.7%; SO_3, 35.3%.

Ammonium N-methylcarbamylsulphamate was prepared by treating an alcoholic solution of the viscous methylurea salt with ammonium hydroxide (80 ml.). Pure ammonium N-methylcarbamylsulphamate was obtained, m.p. 139–140° C. with decomposition. Yield, 80%. Calculated for $C_2H_9O_4N_3S$: N, 24.56%; SO_3, 46.79%. Found: N, 24.8%; SO_3, 46.84%.

Both salts were heated alone and with ammonium sulphamate. The results for ammonium N-methylcarbamylsulphamate are shown in Table X.

TABLE X

AMMONIUM N-METHYLCARBAMYLSULPHAMATE

Molar ratio $CH_3NHCONHSO_3NH_4$: $H_2NSO_3NH_4$	Temp., ° C.	Time in minutes		Yield, %		
		Total	Above 200° C.	Methylguanidine	Guanidine	Cyanuric acid
1:0	200	29	20	Nil	Nil	92.0
1:0	230	29	20	Nil	Nil	50.0
1:0	250	30	20	Nil	Traces	40.0
1:1	200	26	20	34.0	Traces	Traces
1:2	230	26	20	85.0	Traces	Traces
1:2	250	27	20	Traces	57.0	Traces

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THE SYNTHESIS OF PHYLLOPYRROLE-DICARBOXYLIC ACID[1]

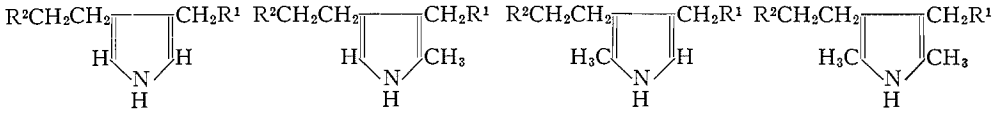
BY S. F. MACDONALD AND K. H. MICHL[2]

ABSTRACT

Phyllopyrrole-dicarboxylic acid, Ic, has been synthesized making all of the four hypothetical reduction products of the uroporphyrins available synthetically.

INTRODUCTION

Two sets of four pyrroles were important both as reduction products of hemin, the coproporphyrins, and the chlorophylls, and as intermediates for synthetic work on these pigments. The first set were basic, opsopyrrole, hemopyrrole, cryptopyrrole, and phyllopyrrole (5*a*), and the second consisted of the corresponding monocarboxylic acids, opsopyrrole-carboxylic acid, etc. (5*b*). Analytically, the members of both sets had been separated as picrates. Work on the uroporphyrins required a third set of dicarboxylic acids, opsopyrrole-dicarboxylic acid, etc. This set was unknown because the reduction products of uroporphyrin I did not form picrates (1).



$R^1 = R^2 = H$:			
Opsopyrrole	Hemopyrrole	Cryptopyrrole	Phyllopyrrole
$R^1 = H$, $R^2 = COOH$:			
Opsopyrrole-carboxylic acid	Hemopyrrole-carboxylic acid	Cryptopyrrole-carboxylic acid	Phyllopyrrole-carboxylic acid
$R^1 = R^2 = COOH$:			
Opsopyrrole-dicarboxylic acid, m.p. 139–140°	Hemopyrrole-dicarboxylic acid, m.p. 150° Hydrobromide, m.p. 160–161° Methyl ester, m.p. 51–52.5°	Cryptopyrrole-dicarboxylic acid, m.p. 126° Hydrobromide, m.p. 137–138° Methyl ester, m.p. 51–53°	Phyllopyrrole-dicarboxylic acid, m.p. 107–108°

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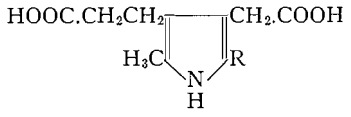
[2]*National Research Laboratories Postdoctorate Fellow, 1953–54.*

Some time ago (11*a*) we modified the standard methods of pyrrole synthesis, which had been inadequate for the syntheses of these dicarboxylic acids, and had provided only ambiguous routes to hemopyrrole-carboxylic acid. The generality of the methods developed is illustrated by the unambiguous syntheses of hemopyrrole-carboxylic acid (11*a*), and of the members of this third set of pyrroles: opsopyrrole-dicarboxylic acid (10), hemopyrrole-dicarboxylic acid (13*a*), cryptopyrrole-dicarboxylic acid (11*b*), and, as now reported, phyllopyrrole-dicarboxylic acid.

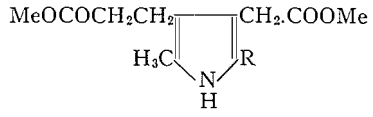
The use of *t*-butyl acetoacetate (15) instead of benzyl acetoacetate in the initial stages implies a similar solution to the general problem; a quite different solution is implied in the synthesis of ethyl α-carbethoxy-cryptopyrrole-dicarboxylate through a Mannich base (16).

The properties of the four dicarboxylic acids explain the analytical difficulties. We have not obtained picrates from opso-, hemo-, or crypto-pyrrole-dicarboxylic acids or from their methyl esters. The methyl esters of hemo- and crypto-pyrrole-dicarboxylic acids are low melting solids, and those of opso- and phyllo-pyrrole-dicarboxylic acids have been obtained only as oils. However, at least hemo- and crypto-pyrrole-dicarboxylic acids are conveniently precipitated as solid hydrobromides (13*b*). All these pyrroles deteriorate unless stored in ampoules sealed under vacuum.

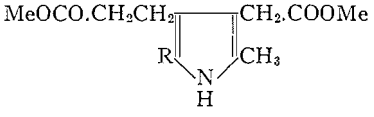
The synthesis of phyllopyrrole-dicarboxylic acid was analogous to that of phyllopyrrole from cryptopyrrole (7*a*). A crude aldimine-hydrochloride was obtained from cryptopyrrole-dicarboxylic acid, I*a*, with hydrogen cyanide and hydrogen chloride. As the isolation of the aldehyde I*b* after the hydrolysis of the intermediate aldimine-hydrochloride was not practicable, the latter was directly reduced by the Wolff-Kishner method (cf. 4) to phyllopyrrole-dicarboxylic acid, isolated as its dimethyl ester, II*c*.



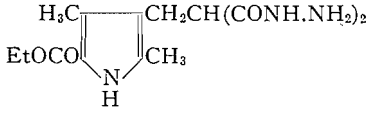
I*a* R = H
b R = CHO
c R = CH_3



II*a* R = H
b R = CHO
c R = CH_3



III*a* R = H
b R = CHO



IV

It was unlikely that this method could be improved through a convenient method of isolating the aldehyde. The latter appeared to show the expected lability in acid solution and high solubility in water. Coupled with this, the hydrolysis of the aldimine-hydrochloride in water was not spontaneous but required alkali, as in closely analogous cases (7*b*).

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The dimethyl esters of cryptopyrrole-dicarboxylic acid and hemopyrrole-dicarboxylic acid, II*a* and III*a*, were therefore treated with hydrogen cyanide and hydrogen chloride. When the resulting aldimine-hydrochlorides were hydrolyzed, the corresponding aldehydes II*b* and III*b* could be isolated. Phyllopyrrole-dicarboxylic acid, I*c*, was obtained by the Wolff-Kishner reduction of II*b*, and its identity confirmed by partial decarboxylation to the known phyllopyrrole-carboxylic acid.

Not unexpected difficulties were encountered in purifying the phyllopyrrole-carboxylic acid (cf. 2, 9) and in obtaining its picrate (cf. 3); if the latter was obtained, the amount was too small for purification and characterization. The purification of the phyllopyrrole-carboxylic acid by repeated vacuum sublimation was inappropriate, causing a lowering of the melting point and an increase in the intensity of the Ehrlich reaction. It may be that the propionic acid group can thus be lost by a reverse of the Michael addition. This may take place on heating pyrroles with potassium methylate (2, 6) and the lability of tetraalkyl pyrroles is such that they apparently lose an alkyl group under the conditions of the Ehrlich reaction (14). In an analogous case, the pyrrolysis of IV to 2,4-dimethyl-5-carbethoxypyrrole (8), the ring is less activated but the split would be facilitated by the extra carboxyl on the side chain and by pyrazolidone formation displacing the pyrrole from the methylene group.

Phyllopyrrole-dicarboxylic acid might have been obtained more directly by heating I*a* with potassium methylate. However, a mixture might then result from the partial replacement of the propionic acid group by methyl (cf. 2, 6). Further, the aldehydes were required for experiments in the synthesis of unsymmetrical dipyrromethenes (12).

EXPERIMENTAL

*2,5-Dimethylpyrrole-3-acetic acid-4-propionic acid Dimethyl Ester (Dimethyl Phyllopyrrole-dicarboxylate), II*c

A suspension of 1.77 gm. of cryptopyrrole-dicarboxylic acid, I*a*, in 6 ml. of absolute ether, 6 ml. of chloroform (alcohol free), and 2 ml. of hydrogen cyanide was cooled in an ice–salt mixture while dry hydrogen chloride was passed in for three hours. After the suspension had been left overnight at 0°, the solvent was removed by a stream of dry air. After being washed with ether, the crude gummy aldimine hydrochloride was heated for 20 hr. at 160° with 0.6 gm. of sodium dissolved in 12 ml. of ethanol and 4 ml. of hydrazine. The tube was washed out with ethanol. After addition of water, the solution was evaporated on the steam bath *in vacuo*; more water was then added and the solution again evaporated. The residue was dissolved in water and chloride ions removed by shaking with freshly prepared silver oxide, then sodium ions were removed by passing the solution through a column of Amberlite IR-120 (hydrogen form, wet weight 20 gm.). Although these operations had been carried out under nitrogen, the solution darkened. The solution was freeze-dried, and the dark brown residue esterified with ethereal diazomethane. The solvent was removed *in vacuo* and the residue distilled twice (130–140°, 5×10^{-5} mm.). On redistilling in a collar flask, the main fraction

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(75 mgm.) was collected at 138–140° (5×10^{-5} mm.) as an easily oxidized pale yellow oil which could not be induced to crystallize; Ehrlich's reaction was negative cold, weakly positive hot. Found: C, 61.78; H, 7.79; N, 5.70%. Calc. for $C_{13}H_{19}NO_4$: C, 61.64; H, 7.56; N, 5.53%.

Methyl Cryptopyrrole-dicarboxylate, IIa

Cryptopyrrole-dicarboxylic acid, I*a*, (3.52 gm.) was esterified with an excess of ethereal diazomethane at 0°. After the ether had been evaporated, the residue was distilled (140–150°, 5×10^{-5} mm.) giving 3.78 gm. (95%) of a slightly yellow viscous oil which solidified in an acetone – dry ice bath, and then had m.p. 51–53°. For analysis it was redistilled in a collar flask, b.p. 136–138° at 10^{-5} mm. Found: C, 60.12; H, 7.15; N, 5.81%. Calc. for $C_{12}H_{17}NO_4$: C, 60.23; H, 7.16; N, 5.86%. It may be stored only *in vacuo* or under nitrogen.

2-Methyl-5-formylpyrrole-4-acetic acid-3-propionic acid Dimethyl Ester, IIb

Methyl cryptopyrrole-dicarboxylate, II*a*, (3.68 gm.) in 22 ml. of absolute ether and 3.7 ml. of hydrogen cyanide was cooled in an ice–salt mixture and dry hydrogen chloride passed in to saturation and for an additional one and one-half hours, the solution being stirred and protected from moisture. The solvent was removed by a stream of dry air, then dry ether twice added to the residue and removed in the same way. The oily product, which crystallized when the residue was left at 0° overnight, was dissolved in 75 ml. of ice water. The cold filtered solution of the imine-hydrochloride was made slightly alkaline by adding aqueous sodium hydroxide very slowly. The product, which separated as a gum, was dissolved in chloroform. The solution was dried with sodium sulphate, filtered, and twice boiled to dryness with absolute ethanol. The solution of the residue in ethanol was warmed with charcoal, filtered, and the solvent evaporated. The dark-colored residue was extracted several times with boiling hexane, the combined extracts concentrated and allowed to cool slowly. The product (1.06 gm., 26%) separated as yellowish needles, m.p. 76.5–77°. For analysis it was recrystallized from pentane (thimble) and distilled (b.p. 100–110°, 10^{-5} mm.) giving long colorless needles, m.p. 78°. Found: C, 58.46; H, 6.18; N, 5.55%. Calc. for $C_{13}H_{17}NO_5$: C, 58.4; H, 6.41; N, 5.24%.

2-Methyl-5-formylpyrrole-3-acetic acid-4-propionic acid Dimethyl Ester, IIIb

Methyl hemopyrrole-dicarboxylate, III*a*, (13*a*) (3.13 gm.) in 9 ml. of ether, 9 ml. of chloroform, and 3.1 ml. of hydrogen cyanide was converted into the crude aldimine-hydrochloride (7.16 gm.) like the isomer above. Here the crude oily product did not crystallize.

(*a*) One hundred and sixty milligrams of this intermediate was dissolved in 10 ml. of water. The solution was filtered, shaken with freshly prepared silver oxide until chloride ions were removed and the reaction was alkaline, filtered quickly, and freeze-dried. When the residue was dissolved in hot hexane and left at 0° overnight, the product (60 mgm., 75%) separated as yellow crystals, m.p. 112–113°. After distillation (110–120°, 5×10^{-5} mm.) and two recrystallizations from hexane (thimble), it formed long colorless needles, m.p. 114–

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114.5°. Found: C, 58.67, 58.59; H, 6.59, 6.50; N, 5.45%. Calc. for $C_{13}H_{17}NO_5$: C, 58.41; H, 6.41; N, 5.24%.

(*b*) The remainder of the intermediate (7.0 gm.) was dissolved in 250 ml. of water. The solution was filtered, cooled, and brought to pH 8 with ammonia, seeded, and left one hour at 0°. The crystalline product was filtered off, dried, recrystallized twice from hexane (thimble), then from 25 ml. of ethanol (charcoal) which was concentrated to 15 ml., seeded, and left at 0° overnight. The product (920 mgm., 27%) formed yellow crystals, m.p. 111–113°.

The dinitrophenylhydrazone, prepared in ethanol, formed clusters of brown rods. Part melted at 198–200°, resolidified at 201°, and then melted with the remainder at 205–207°.

2,5-Dimethylpyrrole-3-acetic acid-4-propionic acid (Phyllopyrrole-dicarboxylic acid), Ic

The aldehyde-ester II*b* (840 mgm.) was heated on the steam bath for one hour with 7 ml. of *N* sodium hydroxide. The solution was filtered into a Carius tube and freeze-dried. After addition of 0.4 gm. of sodium, dissolved in 8 ml. of ethanol, and 2 ml. of hydrazine, the tube was sealed and heated at 160° for 14 hr. The solid in the tube was filtered off, washed with ethanol, dried *in vacuo* at 100°, and dissolved in water, and put through a column of Amberlite IR-120 (hydrogen form, 40 gm. wet weight) under nitrogen. The column was washed with 3 liters of water (boiled, then cooled under nitrogen). The first 250 ml. of effluent contained only silica. The product (394 mgm., 55%) was obtained from the following fractions as very small yellowish crystals, m.p. 107–108° (decomp.), by concentrating *in vacuo* at 20°, then freeze-drying. Ehrlich's reaction was negative cold, very slowly positive hot. Found: C, 58.52; H, 6.49; N, 6.37%; eq. wt. 113.6. Calc. for $C_{11}H_{15}NO_4$: C, 58.65; H, 6.71; N, 6.22%; eq. wt. 112.6.

2,3,5-Trimethylpyrrole-4-propionic acid (Phyllopyrrole-carboxylic acid)

A platinum boat containing phyllopyrrole-dicarboxylic acid, I*c*, (0.16 gm.) was placed in a glass tube and heated under nitrogen. The temperature was brought to 110°, then slowly raised to 122°; decarboxylation was complete in 15 min. The product was then distilled out (115–123°, 5×10^{-5} mm.) as slightly yellowish prisms, m.p. 87–88°, sintering from 86° (Lit.: 88° (3)). Ehrlich's reaction was negative cold, weakly positive hot. It redistilled (112°, 5×10^{-5} mm.) without leaving a residue, giving colorless crystals, m.p. 84–88°, sintering from 81°. Ehrlich's reaction was positive cold. No picrate was formed in ether; in ethanol the amount was insufficient for purification and characterization. Found: C, 66.66; H, 8.27; N, 8.03%; eq. wt. 180. Calc. for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34; N, 7.73; eq. wt. 181.2.

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THE HEAT OF NEUTRALIZATION OF STRONG ACIDS AND BASES IN HIGHLY DILUTE AQUEOUS SOLUTIONS[1]

By H. M. Papee, W. J. Canady, and K. J. Laidler

ABSTRACT

Heats of neutralization of sulphuric and hydrochloric acids by sodium hydroxide have been determined, using a microcalorimeter of the Tian–Calvet type. The range of concentrations employed was 5×10^{-4} N to 3×10^{-2} N, which is sufficiently low to permit an accurate extrapolation to be made down to zero concentration. The extrapolated values obtained were: for H_2SO_4–NaOH, 13.48 $\pm$0.05 kcal. per gm-equiv. and for HCl–NaOH, 13.52$\pm$0.05 kcal. per gm-equiv. These values, which correspond to the process $H_3O^+ + OH^- \rightarrow 2H_2O$, are significantly higher than the values of 13.32–13.37 kcal. obtained on the basis of previous calorimetric studies in a much higher concentration range. The present values, however, agree well with those calculated by Harned and co-workers and by Everett and Wynne-Jones from electrochemical data.

INTRODUCTION

Although heats of neutralization of strong acids by strong bases have been measured on very many occasions, there has remained a distinct discrepancy between the results obtained by direct calorimetry and those calculated from electrochemical data. The classical calorimetric studies of this problem are those of Richards and Rowe (12) and of Richards and Hall (11), who worked with a variety of strong acids and bases, at concentrations (after mixing) of 1 M and higher. Various workers, including Rossini (13), Pitzer (10), and Kegeles (8), have employed heat of dilution and other thermochemical data to calculate from Richards' results the heat of neutralization at infinite dilution and at 25° C., and have obtained values ranging from 13.32 to 13.37 kcal. per gm-equiv.* Pitzer (10) also made a calorimetric determination of his own from which he obtained a value of 13.36$\pm$0.016 kcal. per mole at infinite dilution. Later calorimetric determinations at higher concentrations, such as those of Bender and Bierman (1) and of Bierman and Weber (2), have provided some support for the 13.32 value.

The value for the heat of neutralization at infinite dilution is the heat of the process $H_3O^+ + OH^- \rightarrow 2H_2O$, and may also be obtained from the temperature dependence of the e.m.f. of various cells. Harned and Owen (6) analyzed the results of such experiments and arrived at a value of 13.48 kcal. for the process. Using somewhat more reliable methods of analysis of the same results, Everett and Wynne-Jones (5) and Harned and Robinson (7) arrived at values of 13.49 and 13.51 kcal. respectively. The probable errors of the electrochemical values are about 0.05 kcal.; those of the calorimetric values are more difficult to estimate, since they involve corrections for dilutions. The calorimetric values are seen to be lower than the electrochemical ones by 0.15 to 0.2 kcal., which is outside the range of errors of the electrochemical values.

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Contribution from the Department of Chemistry, University of Ottawa, Ottawa, Canada.
**All calories quoted in this paper are "thermochemical" calories, equal to 4.1840 absolute joules.*

The weakness of the previous calorimetric work is that, in order for the heats liberated to be sufficiently large to be measured accurately, the determinations must be made at fairly high concentrations, and under these conditions the corrections for dilution are substantial. With the use of modern microcalorimetric techniques it is, however, possible to make determinations of heats of neutralization at very much lower concentrations than have hitherto been employed. The microcalorimeter employed in the present investigation is of the Tian–Calvet type, and is capable of making accurate ($\pm 0.5\%$) measurements of heats as small as 5×10^{-2} small calories. With samples of 10 ml. this means that accurate measurements can be made of heats of neutralization down to concentrations of about 5×10^{-4} M. The use of such techniques clearly eliminates the necessity of employing heat of dilution data, and permits the value at infinite dilution to be obtained by a short extrapolation.

The present communication describes work on the heats of neutralization of sulphuric acid and sodium hydroxide, and of hydrochloric acid and sodium hydroxide, at concentrations (after mixing) ranging from 5×10^{-4} N to 3×10^{-2} N. The present investigation is part of an extensive program of microcalorimetry which will include studies of heats of neutralization of acids and bases of various kinds. The work done so far has been with substituted phenols (9), substituted anilines, aliphatic acids, and substituted benzoic acids; the results with the latter compounds will be published in due course.

EXPERIMENTAL

The microcalorimeter employed was of the type originally designed by Tian (14) and later modified by Calvet (3, 4) by the introduction of a differential system that increased the sensitivity. The instrument consists essentially of a central aluminum block containing four cells, to each of which 144 iron–constantan thermocouples are attached. These are connected differentially to a high sensitivity galvanometer and a switching arrangement which provides three sensitivities. The instrument was used at its highest sensitivity when heats of 0.01 to 0.4 calories were being measured, at medium sensitivity for heats of 0.4 to 2 calories, and at low sensitivity for heats of over 2 calories. This calorimeter being of the conduction type, the results are independent of the specific heat of the solutions involved.

Tian (14) proved that the heat evolved is a function of (and very nearly proportional to) the area of the curve showing galvanometer deflection against time. These deflections were recorded by means of a Beckman "Photopen" photoelectric light-spot follower. The areas were measured using a planimeter. Calibration was carried out by passing a known number of joules of electricity through a manganin resistor immersed in liquid in the calorimeter cell. Absolute joules were converted into calories by means of the factor 4.1840 joules per calorie, and the calories quoted in this paper are therefore the "thermochemical" calories employed in the U.S. National Bureau of Standards compilations. Heat measurements with the instrument were found to be reproducible to within 0.5%.

The sulphuric and hydrochloric acids, and the sodium hydroxide, were

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C.P. reagents. The sodium hydroxide solution was standardized against oxalic acid, and the sulphuric and hydrochloric acid solutions against the sodium hydroxide. Stock solutions were made and were diluted as required.

The procedure was to mix, in the cell of the calorimeter, 0.5 ml. of a solution of the acid with 9.5 ml. of a sodium hydroxide solution. The acid concentration was varied over such a range that the final concentration of the acid in the mixture (before neutralization) was from 5×10^{-4} N to 3×10^{-2} N. The alkali concentration was adjusted so as always to be in considerable excess; it was found by direct test that the actual concentration had no effect on the heat evolved. The alkali solution was placed in the main cell of the calorimeter, which was coppered on the outside to ensure good heat conduction to the block. The acid solution, delivered from a micropipette capable of an accuracy of 0.02%, was contained in a small glass bulb with a thin projection at its base.

The calorimeter is in a specially built insulated room maintained at 25.0 $\pm$0.1° C. and a relative humidity of about 5%. Before being mixed the solutions were allowed to come to thermal equilibrium. Mixing was achieved by breaking the projection on the bulb, and complete mixing brought about by the manipulation of a rubber ball connected to the bulb. In all cases a blank was run simultaneously in another cell of the calorimeter; 0.5 ml. of acid solution was mixed with 9.5 ml. of water instead of alkali solution. This allows for the effects of dilution (actually negligible at these concentrations) and for the heat developed in the mixing operations.

RESULTS

The heats evolved are shown plotted against the acid concentrations in Figs. 1 and 2. In both systems the total spread of values is about 0.1 kcal., or less than 1% of the total. Application of the method of least squares led to the following values for the intercepts on the heat axes, i.e. for the heats at infinite dilution:

H_2SO_4–NaOH, $\Delta H^\circ = -13.52\pm0.06$ kcal. per gm-equiv.

HCl–NaOH, $\Delta H^\circ = -13.48\pm0.05$ kcal. per gm-equiv.

The difference between the two values is clearly of no significance, and the average value of

$$\Delta H^\circ = -13.50\pm0.05 \text{ kcal. per mole}$$

may therefore be taken as the value provided by the present investigation for the process $H_3O^+ + OH^- \rightarrow 2H_2O$ at 25.0° C. and infinite dilution.

The plots show that there is very little variation of ΔH with concentration over the range investigated. The least squares treatment leads to the following values for the slopes:

H_2SO_4–NaOH, 1.7$\pm$1.0 kcal. per gm-equiv./gm-equiv. per liter.

HCl–NaOH, 2.2$\pm$1.0 kcal. per gm-equiv./gm-equiv. per liter.

These slopes correspond to a scarcely significant rise in heat over the range investigated.

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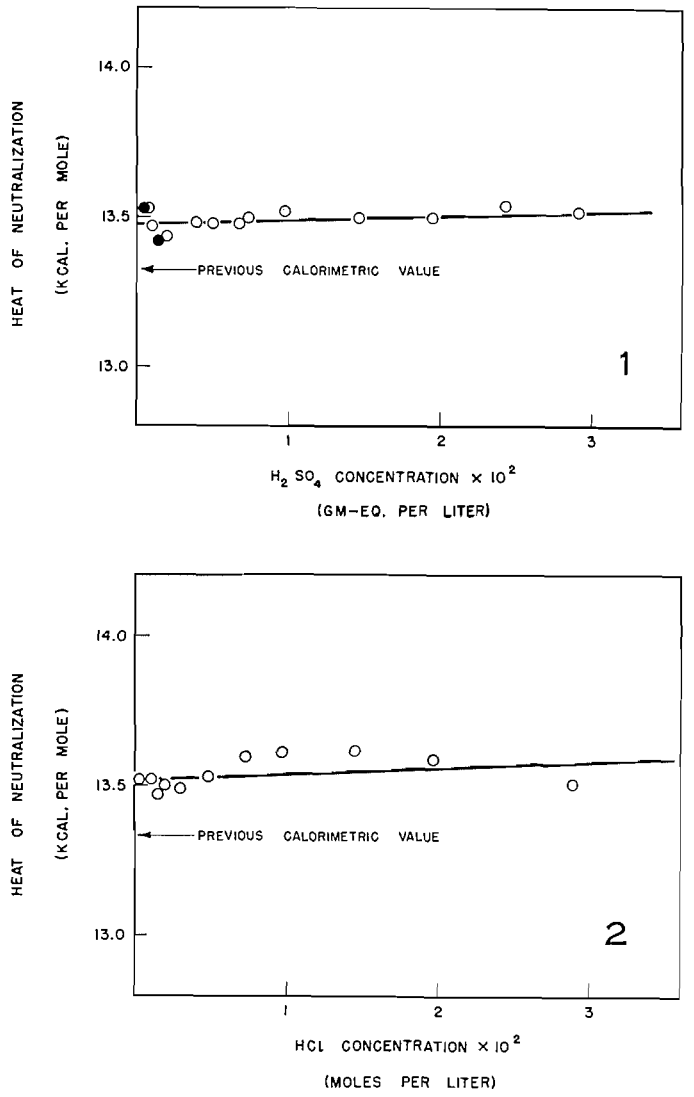

FIGS. 1 and 2. Plots of heat of neutralization against acid concentration for the sulphuric acid – sodium hydroxide system and the hydrochloric acid – sodium hydroxide system; $T = 25.0°$ C.

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DISCUSSION

The heat of neutralization obtained in the present investigation, 13.50 kcal. per mole at infinite dilution, is consistent with the values of 13.48–13.51 obtained from the electrochemical data. It is, however, definitely higher than previous calorimetric values (13.32–13.37). The difference is outside the range of error of the present investigation and of the electrochemical work. The errors inherent in the previous calorimetric work are difficult to assess but are probably larger since the final value depends upon the application of several corrections for dilution.

It is of interest in this connection to see how the value obtained in the present investigation fits in with those obtained at higher acid concentrations. Kegeles (8) has applied various corrections to the results of Richards and coworkers (11, 12), and some of his corrected heats are plotted against concentration in Fig. 3. It is to be seen that the infinite dilution value obtained in the present investigation lies on a smooth curve connecting the higher concentration points, but that the lower values given by the previous calorimetric studies require an inflection in the curve.

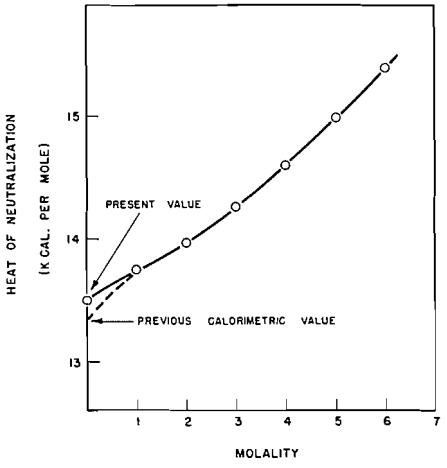

FIG. 3. Plot of the values for the heat of neutralization of hydrochloric acid by sodium hydroxide; the points at the higher concentrations were calculated by Kegeles from the data of Richards *et al.*

The microcalorimeter employed in these investigations was installed at the University of Ottawa by Professor P. R. Gendron, Dean of the Faculty of Science. Pressure of other duties has prevented Professor Gendron from using this instrument, and we cannot express too strongly our appreciation to him for turning it over to our use and for his never-failing encouragement and assistance with regard to its operation.

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DIMETHYLPHENYLBENZYLAMMONIUM CHLORIDE: A REAGENT FOR THE GRAVIMETRIC DETERMINATION OF PLATINUM[1]

By D. E. Ryan

ABSTRACT

Dimethylphenylbenzylammonium chloride precipitates platinum quantitatively from tetravalent platinum bromide solutions; complete precipitation is obtained in solutions varying widely in concentrated hydrobromic acid. The compound formed is a stable ammonium type salt, $(C_{15}H_{18}N)_2PtBr_6$, and is used as a weighing form for platinum. Commonly associated base metals do not interfere. Platinum is readily determined in filtrates from hydrolytic separation of other platinum metals.

INTRODUCTION

The separation and determination of small quantities of platinum, even from solutions containing platinum only, is rather difficult; a comparative study of the microgravimetric methods for determining platinum (1) emphasizes the need for more suitable procedures. Since all methods previously described require ignition to the metal with its attendant disadvantages as a weighing form, investigations were carried out to find an organic reagent that would precipitate platinum quantitatively in a form that could be dried at 110° C. and weighed.

In a previous paper (3) it was stated that either addition compounds or, because of the marked stability of $MX_6^=$ anions, ammonium type salts would generally be precipitated from solutions of the *tetravalent* platinum metals. To precipitate ionic solids, as ammonium hexachloroplatinate, from solution it is necessary that the lattice energy of the crystal be greater than the hydration energy of the ions involved; the greater the difference between the lattice energy and the hydration energy the more complete the precipitation. The hydration energy can be decreased by increasing the size of the ions and—provided the lattice energy is not more adversely affected (by the increase in interionic distance or a change in crystal structure)—it should be possible to obtain more insoluble haloplatinates by substituting large ammonium type cations for the ammonium ion. Strychnine and brucine, for example, do give much more insoluble chloroplatinates but poor precision and necessity for close pH control limit their usefulness. The quaternary ammonium salt dimethylphenylbenzylammonium chloride, however, precipitates small amounts of platinum from solutions of widely varying acidities in a form that can be dried at 110° C. and weighed.

[1]*Manuscript received August 7, 1956.*
Contribution from the Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, with financial assistance from the National Research Council, Ottawa, Canada.

EXPERIMENTAL

Preparation of Reagent

Dimethylphenylbenzylammonium chloride, $(CH_3—\underset{\displaystyle C_6H_5}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{N}}}}—CH_2C_6H_5)Cl$, was prepared by simply mixing equimolar amounts of benzyl chloride and dimethylaniline and allowing the mixture to stand at ordinary temperatures until a crystalline mass was formed. The solid was washed with ether to remove unchanged benzyl chloride and dimethylaniline. A white crystalline product was obtained when the solid was dissolved in alcohol and recrystallized by the addition of ethyl acetate.

Properties

Dimethylphenylbenzylammonium chloride is a white crystalline solid melting at 110° C. It is readily soluble in water and 5% aqueous solutions have been kept, in a dark bottle, for several months with no sign of decomposition.

No noticeable reaction is obtained upon addition of reagent solution to 0.05 *M* solutions of the following ions acidified by hydrochloric or hydrobromic acids: $Cu^{\cdot\cdot}$, $As^{\cdot\cdot\cdot}$, $As^{\cdot\cdot\cdot\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, $Co^{\cdot\cdot}$, $Ni^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, $Cr^{\cdot\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Ba^{\cdot\cdot}$, $Ca^{\cdot\cdot}$, $Sr^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, $UO_2^{\cdot\cdot}$, $Ti^{\cdot\cdot\cdot\cdot}$, $Zr^{\cdot\cdot\cdot\cdot}$, $Th^{\cdot\cdot\cdot\cdot}$, $Ce^{\cdot\cdot\cdot\cdot}$. Voluminous pale yellow precipitates are obtained with $Bi^{\cdot\cdot\cdot}$ and $Sb^{\cdot\cdot\cdot}$ whilst $Cd^{\cdot\cdot}$, $Hg^{\cdot\cdot}$, and $Sn^{\cdot\cdot\cdot\cdot}$ give a small amount of white precipitate. Lead does not react with the reagent but the halide is formed when its solubility is exceeded.

Reaction occurs, as shown by the immediate formation of a precipitate, with dilute acid solutions of ClO_4', MoO_4'', WO_4'', Cr_2O_7'', VO_4''', and $Fe(CN)_6''''$; no precipitates are formed with Cl', Br', $C_2H_3O_2'$, NO_3', CNS', IO_4', CO_3'', C_2O_4'', PO_4''', and $Fe(CN)_6'''$. Bromine and reagent solution produce a yellow precipitate.

The following results are obtained with chloride solutions of the platinum metals: $Pd^{\cdot\cdot}$—pink precipitate, $Os^{\cdot\cdot\cdot\cdot}$—yellow precipitate, $Ir^{\cdot\cdot\cdot\cdot}$—brown precipitate, $Pt^{\cdot\cdot\cdot\cdot}$—yellow precipitate, $Rh^{\cdot\cdot\cdot}$—no noticeable reaction.

Reaction with Platinum

Hydrous platinic oxide ($PtO_2.xH_2O$) was prepared by the addition of sodium hydroxide to platinic chloride solutions and precipitation with acetic acid. The results obtained upon addition of reagent to solutions of this oxide in various acids are of interest. Fluffy, yellow, needle-like crystals were slowly precipitated from nitrate solutions. A small amount of pale yellow precipitate dispersed throughout the solution was obtained with sulphate. The white crystalline product obtained from platinum perchlorate solutions was due to the reaction between reagent and perchloric acid. Cyanide solutions gave a small amount of crystalline white precipitate. From chloride solutions there was immediate precipitation of a yellow complex whilst from platinic bromide an orange precipitate was obtained.

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Complete precipitation was approached only in the platinum halide solutions. Results obtained from standard $PtCl_6^=$ solution were consistent but about 0.2 mgm. low on 10 mgm. samples taken for analysis. From $PtBr_6^=$ solutions, however, complete precipitation was obtained even in solutions containing 30% of concentrated hydrobromic acid; as little as 0.05 mgm. of platinum in 100 ml. of solution (0.5 p.p.m.) gave a noticeable reaction.

The compound precipitated from tetravalent platinum halide solutions is the ammonium salt $[(CH_3)_2(C_6H_5)N(CH_2C_6H_5)]_2PtX_6$. The compound obtained from platinic chloride solutions was found to contain 23.50% platinum (theoretical 23.45%) whilst that from bromide solutions gave 17.77% (theoretical 17.76%). The bromide complex has a melting point of 167–168° C.; it can be dried at 110° and used as a form in which to weigh platinum with the favorable factor of 0.1776.

Standard Platinum Solutions

Platinum solutions were prepared from pure platinum sponge obtained from Johnson, Matthey, and Mallory, Ltd. Weighed samples of the sponge were dissolved in aqua regia and the solutions evaporated on the steam bath. The samples were then evaporated to dryness three times with concentrated hydrochloric or concentrated hydrobromic acids, depending on whether a $PtCl_6''$ or a $PtBr_6''$ standard solution was desired. The residue was then taken up in dilute hydrochloric or hydrobromic acid, the solution filtered into a volumetric flask, and diluted to the mark.

Procedure

Samples of platinic bromide were diluted to 100 ml. and varying amounts of bromine free concentrated hydrobromic acid added. Five milliliters of a 5% aqueous solution of dimethylphenylbenzylammonium chloride was added, with stirring, for each 10 mgm. or less of platinum present. The samples were left at room temperature for three hours, then filtered through porous-based porcelain crucibles, washed with a 0.1% aqueous reagent solution, and dried at 110° C. The weight of the precipitate was multiplied by the theoretical factor 0.1776 to obtain the weight of platinum. The results are shown in Table I.

These results show that platinum can be precipitated quantitatively from platinum bromide solutions containing widely varying amounts of hydrobromic acid by dimethylphenylbenzylammonium chloride in a form that can be dried at 110° and weighed. Excellent results are obtained from nitrate and chloride solutions converted to the bromide by evaporating on the steam bath in the presence of sodium bromide or hydrobromic acid. Lead does not interfere unless the solubility of lead bromide is exceeded nor do most base metals.

Other platinum metals can be removed by hydrolytic precipitation (2) and the platinum determined in the filtrate without difficulty. The filtrate, in this instance, is evaporated to dryness, bromate carefully destroyed with hydrochloric acid and then evaporated again on the steam bath in the presence of hydrobromic acid to ensure complete conversion to $PtBr_6^=$. The sample is then diluted, filtered, reagent added, and the filtered complex weighed as before.

TABLE I

PRECIPITATION OF PLATINUM BY DIMETHYLPHENYLBENZYLAMMONIUM CHLORIDE AND WEIGHING AS THE COMPLEX $(C_{15}H_{18}N)_2PtBr_6$

Pt taken, mgm.	Pt recovered, mgm.	Remarks
1.08	1.08	Solution 0.5% in concentrated HBr
1.34	1.32	"
5.38	5.36	"
10.06	10.05	"
21.52	21.52	"
10.76	10.76	"
10.76	10.76	Solution 1% in concentrated HBr
10.76*	10.78	Solution 2% in concentrated HBr
10.76*	10.76	Solution 2% in concentrated HBr
10.76	10.76	Solution 5% in concentrated HBr
10.76	10.78	Solution 30% in concentrated HBr
10.86	10.88	$PtCl_6''$ solution + 5 gm. NaBr evaporated to dryness, diluted, and platinum precipitated
10.86	10.86	$PtCl_6''$ solution + 10 ml. concentrated HBr evaporated, diluted, and platinum precipitated
10.86	10.88	20 mgm. Pb present
10.86	10.88	20 mgm. Pb + 20 mgm. Fe present
10.86	10.85	10 mgm. each of Pb, Fe, Cu, Ni, and As present
10.86	10.84	10 mgm. total of Ir, Rh, Pd present was first removed by hydrolytic precipitation and platinum determined in filtrate after destruction of bromate and conversion to bromide
10.86	10.86	"

**These results were obtained independently by C. A. Armour, a member of this laboratory.*

Dimethylphenylbenzylammonium chloride—easily prepared from dimethylaniline and benzyl chloride—should prove to be a useful reagent for the gravimetric determination of platinum; the favorable factor for the compound precipitated from bromide solutions and the volume of precipitate obtained is an asset when dealing with small amounts of platinum.

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MEASUREMENT OF PRESSURES IN THE TITANIUM IODINE SYSTEM USING THE EFFUSION METHOD[1]

By A. Herczog[2] and L. M. Pidgeon[3]

ABSTRACT

The equilibrium vapor pressures of TiI_4 and TiI_2, obtained by the simultaneous decomposition and evaporation of TiI_2 in the presence of excess Ti, have been measured over the temperature range 750–902° K. using the effusion method. Thermodynamic data have been calculated for the equilibrium systems:

$$2TiI_2(s) = Ti(s) + TiI_4(g),$$
$$TiI_2(s) = TiI_2(g).$$

In the purification of titanium by the Van Arkel–de Boer "hot wire" method, the metal is carried as a volatile titanium iodide. While the method has been employed extensively, little work has been reported covering vapor pressure determinations at elevated temperatures. Blocher and Campbell (1) have measured the vapor pressure of titanium tetraiodide, while Fast (5) has generally investigated the titanium–iodine system. Degassed titanium reacts with iodine vapor even at room temperature with formation of the tetraiodide, di-iodide being formed as an intermediary step. At temperatures above 200° C., where the vapor pressure of the tetraiodide is appreciable, it reacts with titanium to form a di-iodide, and the latter reacts with tetraiodide to form the tri-iodide. Above 350° C., the tri-iodide disproportionates in vacuum as follows:

$$2TiI_3(s) = TiI_2(s) + TiI_4(g).$$

In the presence of an excess of titanium, the tetraiodide vapor formed by disproportionation of the tri-iodide reacts with titanium to form di-iodide so that in equilibrium conditions, all the iodine present in the system is converted to di-iodide.

It is interesting to observe that in the case of titanium trichloride the conditions are different. While the tri-iodide decomposes without evaporation, the trichloride vaporizes and decomposes simultaneously. An investigation of the disproportionation and vapor pressure of the lower chlorides of titanium has been done by Farber and Darnell (4) and by Skinner and Ruehrwein (9).

Above 480° C., the di-iodide vaporizes and decomposes simultaneously according to

$$TiI_2(s) \rightarrow TiI_2(g);\ 2TiI_2(s) \rightarrow Ti(s) + TiI_4(g).$$

In this system at 480° C. or higher, titanium and the di-iodide are the only solid phase components, while in the vapor phase only di-iodide and tetraiodide are present. The purpose of the present investigation was to determine the partial pressures of the gas phase under equilibrium conditions.

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Contribution from the Department of Metallurgical Engineering, University of Toronto, Toronto, Ontario. Published with permission of the Defence Research Board of Canada.
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[3]*Professor of Metallurgical Engineering, University of Toronto.*

EXPERIMENTAL METHOD

In order to measure the partial pressures, a spectrophotometric method (11) was first considered, but was soon abandoned because of the formation of non-transparent titanium deposits on the walls of the container. The effusion method and the entrainment method were then considered. In both cases, the vapor pressure measurement is based on the analysis of condensed vapors and involves the manipulation of substances which are extremely sensitive to contamination by water vapor and by oxygen. When the entrainment method was used, the danger of contamination appeared to be higher because of the large quantities of inert gas flowing through the system. Another difficulty of the entrainment method involves choosing the correct flow rate of the inert gas for two vapor components. This rate must be low enough to allow saturation to be achieved but high enough to avoid forward diffusion. It was decided, therefore, to use the effusion method and to use a manometric method to check the calculated total pressure independently.

Effusion Apparatus

The apparatus is shown in Fig. 1. The substance is contained in a Knudsen cell constructed of titanium metal, and is heated under vacuum in a 1 in.

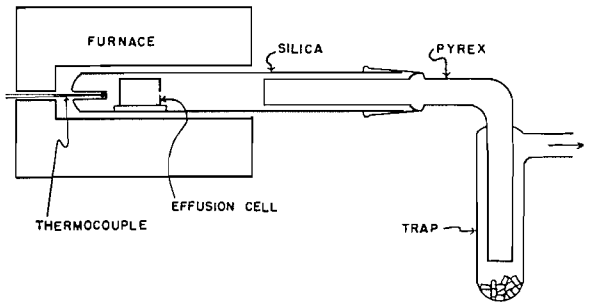

FIG. 1. Diagram of apparatus.

silica tube connected with a ground joint to the rest of the apparatus made from pyrex glass. The titanium di-iodide vapor condensed in the silica tube at the end of the furnace. Some tri-iodide was also found, very likely formed by reaction of the di-iodide with tetraiodide vapor after effusion from the cell. The rest of the tetraiodide vapor was condensed in the liquid air trap containing glass rings at the bottom to increase the condensation surface. The smallest internal diameter of the apparatus was $\frac{3}{4}$ in. The residual vacuum measured by a McLeod gauge was of the order of 10^{-6} mm. The vacuum was produced by a three-stage mercury pump. A second liquid air trap (not in figure) was used to prevent the condensation of mercury in the apparatus. After the runs, the apparatus was filled with argon, which had been dried with magnesium perchlorate and purified over a titanium getter (8). The silica tube with the liquid air trap was now taken off from the rest of the equipment and the open end closed with a rubber stopper while argon was flowing through the system. With a rubber gasket around the outer part of the ground joint,

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the silica tube was inserted into the lock of a dry box manipulator. The lock and the apparatus were evacuated and refilled with purified argon from a 1-gal. heavy-walled rubber bag used for storage of argon and for keeping the dry box under pressure. Then the internal vacuum-tight cover of the lock was opened, the silica tube pulled into the dry box, the cell transferred to a weighing glass, and the silica tube replaced into the ground joint. Subsequently, the apparatus with the condensed iodides and the weighing glass with the cell were removed from the lock, the cell weighed, and the condensed iodides in the apparatus analyzed. The cell was then transferred in another apparatus by dry box manipulation and attached to the vacuum system for the next run.

Preparation of the Sample and Analysis

Filings of iodide titanium were prepared under argon. The titanium was placed in the apparatus shown in Fig. 2, degassed at 800° C. under high vacuum, and sealed off from the pump.

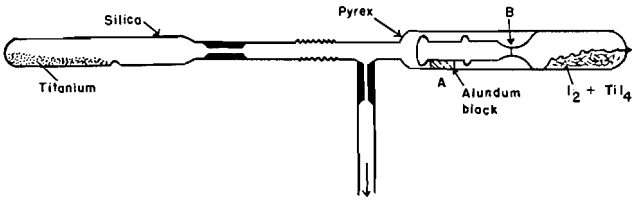

FIG. 2. Diagram of apparatus for the preparation of TiI_2.

Iodine and a small quantity of titanium powder were placed in the evacuated ampoule provided with a breakable joint and heated to vaporize the contents. By this procedure, a small quantity of tetraiodide was produced with the object of eliminating traces of moisture or of oxygen from the iodine. After the titanium was degassed, the joint was broken at (B) in the vacuum system by judicious heating at (A), which collapsed the glass wall under atmospheric pressure. The iodine distilled to the silica tube containing the degassed titanium. The container, after being sealed off, was kept for several days at 440° C. in order to complete the conversion to di-iodide. The reaction was followed by pulling out one end of the container from the furnace to observe any condensation of tetraiodide, which would indicate the presence of tri-iodide. The silica container was then opened in the dry box, the contents crushed, and transferred to the cell. The cell contained approximately 1.5 gm. titanium and 1.7 gm. titanium di-iodide. Four samples were prepared for all runs.

At the end of the run, the iodides condensed in the apparatus were dissolved in 5% sulphuric acid and the solution was precipitated with ammonia. The precipitate was dissolved in hot 5% sulphuric acid; the solution after reduction with nascent hydrogen and collection in a ferric solution was titrated with $N/20$ $KMnO_4$. The filtrate was acidified with acetic acid and titrated with $N/20$ $AgNO_3$ solution using eosin as an adsorption indicator according to Fajans (3). The iodine analysis was sufficiently exact for all cases, but the volumetric method used for titanium when the smallest quantities were being

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determined was replaced by a colorimetric method. The analytical results agreed, within the experimental error, with the loss in weight of the cell.

Experimental Results

For the effusion method, the vapor pressure is calculated from the formula of Knudsen (7)

$$P = (m_t/K.A)\sqrt{2\pi RT/M},$$

where m_t is the effusion rate per unit of time, A the area of orifice, M the molecular weight, and K a correction factor for the wall thickness of the orifice. For P expressed in mm., the effusion rate m_t in mgm./hr., and all other quantities in c.g.s. units, the following formula is obtained:

$$P = (4.76\times10^{-6}\, m_t/KA)\sqrt{T/M}.$$

This equation was used to calculate the partial pressures either of the TiI_2 vapor or of the TiI_4 vapor by inserting the appropriate values of m_t and of M. Three different sizes of orifice were used, as shown in Table I, where the critical dimensions are: A, area; l, wall thickness; a, radius of the orifice; and K, the correction factor (calculated according to Clausing (2)). The results of the experiments are given in Table II, and the values of log P are plotted against 1/T in Fig. 3.

TABLE I

Orifice No.	A, cm.^{2}	l, cm.	a, cm.	K
1	0.0177	0.0356	0.0751	0.81
2	0.0095	0.0326	0.0550	0.77
3	0.00256	0.0228	0.0285	0.72

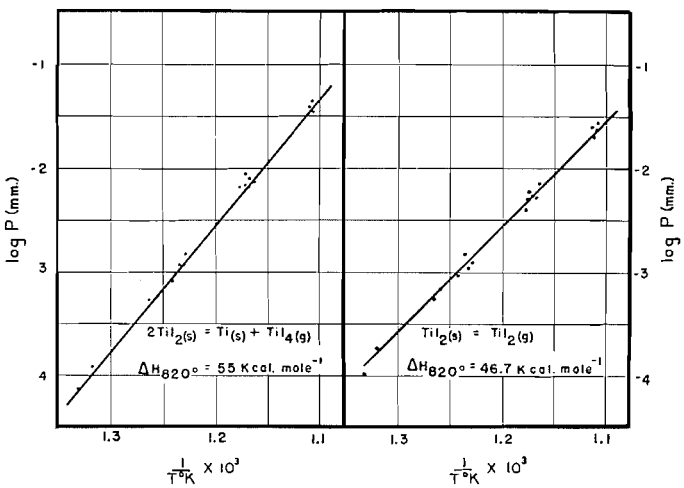

FIG. 3. Plot for the calculation of ΔH.

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TABLE II

$T°$, K.	Time, hr.	Orifice No.	Effused material, mgm./hr. TiI_4	Effused material, mgm./hr. TiI_2	P TiI_4 $\times 10^3$ mm.	P TiI_2 $\times 10^3$ mm.
750	91.3	1	0.19	0.19	0.073	0.10
758	22.0	1	0.31	0.34	0.12	0.18
791	27.2	1	1.33	1.02	0.53	0.55
795	22.8	1	1.42	1.25	0.56	0.68
805	22.0	2	1.05	0.83	0.82	0.88
810	19.0	1	2.88	2.73	1.16	1.49
811	21.0	2	1.47	1.01	1.15	1.08
813	18.4	1	3.70	2.15	1.49	1.18
850	16.4	2	8.11	3.65	6.51	3.96
852	2.0	1	15.92	9.08	6.55	5.08
853	4.7	2	10.78	5.43	8.67	5.92
854	7.8	2	8.22	4.77	6.61	5.19
856	16.2	3	2.46	1.21	7.91	5.27
859	2.0	1	17.28	12.97	7.11	7.25
900	3.5	3	9.88	5.85	32.6	26.2
901	2.0	2	46.11	17.78	38.1	20.0
902	2.0	2	53.05	24.57	43.9	27.5
902	15.0	3	10.27	4.98	33.9	22.3

DISCUSSION

To calculate the partial pressures from the analyzed quantities of iodine and titanium, the basic assumption has been made that the effusing vapor consists of TiI_2 and TiI_4 molecules only. This assumption is based on the fact that under equilibrium conditions in the presence of an excess of titanium, TiI_2 is the only stable compound in the solid phase (at temperatures above 350° C.) and at higher temperatures the di-iodide sublimes and simultaneously decomposes according to the reaction

$$2TiI_2(s) = Ti(s) + TiI_4(g).$$

Another possible reaction for the decomposition of TiI_2

$$3TiI_2(s) = Ti(s) + 2TiI_3(g)$$

has not been considered because (and this is a basic difference from the behavior of titanium chlorides) there is no experimental evidence that TiI_3 vapor can be produced. TiI_3 crystals decompose without evaporation to $TiI_2(s) + TiI_4(g)$, as observed at lower temperature. However, it is possible that, at higher temperatures, in the presence of a higher pressure of TiI_4 and TiI_2 vapor, the conditions of stability for TiI_3 vapor are improved. The question of whether or not TiI_3 is present in the vapor phase cannot be decided by chemical analysis of the effused vapors because the di-iodide may react with the tetraiodide vapor after the effusion at lower temperature with formation of tri-iodide. Since no other experimental data are available, and no heat of formation of the iodides is known, the question remains undecided. However, it is considered unlikely that under the present experimental conditions TiI_3 vapor was present in appreciable quantities. The presence of TiI_3 vapor, if any, would decrease the partial pressures and the ΔH values both for the sublimation and the decomposition of TiI_2.

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The measurements of the sublimation and decomposition pressure of TiI_2 in the presence of an excess of titanium were performed over a range of temperature from 750 to 902° K. The sublimation pressure varied from 0.0001 to 0.027 mm. and the decomposition pressure from 0.000073 to 0.044 mm. The lower limit was determined by the time necessary to produce sufficient quantities of effused material for analysis and the higher limit by the condition of free molecular flow within the experimental error. The measured residual pressure was of the order of 10^{-6} mm. The furnace temperature was controlled with a regulator to ± 2 to ± 4° C. for runs of one or more days. Since the effused quantities of TiI_2 and TiI_4 are calculated from analytical values of titanium and iodine, a small error in the determination of the smaller quantity (titanium) produces a larger error in the ratio TiI_2/TiI_4. Great care was taken to avoid contamination of the material with water vapor and atmospheric gases because it was found that smallest quantities of oxygen (10) in the form of a surface contamination have a long-lasting effect on the equilibrium pressure.

The thermodynamic functions reported in Table III have been calculated from the experimental data using the "Σ-plot" method described by Kelley (6). The specific heat functions required for the calculation have been estimated by comparison with other molecules, especially chlorides of titanium and chlorides and iodides of other metals, whose properties are known. The details of the method of estimation, although simple enough in principle, are too tedious for discussion here.

TABLE III

	Decomposition $2TiI_2(s) = Ti(s) + TiI_4(g)$	Sublimation $TiI_2(s) = TiI_2(g)$
ΔC_p, cal./mole	$-3.6-4.2\ T.10^{-3}$	$-1.75-2.6\ T.10^{-3}$
ΔH, "	$59{,}400-3.6\ T-2.1\ T^2.10^{-3}$	$49{,}000-1.75\ T-1.3\ T^2.10^{-3}$
$\Delta F°$, "	$59{,}400+3.6\ T \ln T$ $+2.1\ T^2.10^{-3}-72.9\ T$	$49{,}000+1.75\ T \ln T$ $+1.3\ T^2.10^{-3}-46.6\ T$
ΔH_{298}, kcal./mole	58.1	48.4
ΔS_{298}, e.u.	47.3	34.2

ACKNOWLEDGMENT

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THE ADSORPTION OF NITROGEN BY BROMINATED CHARCOAL[1]

By H. L. McDermot

ABSTRACT

The adsorption of nitrogen has been measured at 78° K. for two charcoals which have been brominated and heat-treated at a variety of temperatures. In no instance did removal of the sorbed bromine by heat-treatment bring about activation of the charcoal. The "densities" of bromine sorbed by charcoal have been calculated from the volumes of nitrogen sorbed by charcoal containing varying amounts of residual bromine. In all cases, the "density" of sorbed bromine was found to be less than that of solid bromine.

INTRODUCTION

In an earlier paper (4), experimental work was presented on the adsorption of nitrogen by a series of brominated graphites and by one brominated carbon black. It was shown that for all the carbons, the surface area as measured by nitrogen adsorption gradually increased as bromine was removed. However, the carbons behaved differently after all the bromine was removed by treatment at high temperatures. In the case of the graphites, the surface area measured after heat-treatment at 1000° C. appeared to be related to the crystallite size of the untreated graphite. Thus the surface area of the graphite of largest crystallite size after bromination and heat-treatment at 1000° C. was found to be less than that of the starting material. After the same treatment, the area of the graphite of smallest crystallite size was observed to be greater than that of the original material, i.e., it had clearly been activated by the combination of bromination and heat-treatment. Similar results were obtained with a carbon black after bromination and heat-treament at 600° C. In both cases of activation, the increase in surface area was evidently achieved by a reduction in particle size, because in neither case was there evidence of an increase in porosity of the carbon.

Activated charcoal consists of crystallites which are more highly disorganized than those of the graphites. The carbon planes of the crystallites have approximately the same c spacing as those of graphites, but are randomly oriented around a perpendicular to the planes. These crystallites are formed at an early stage in a high temperature activation process before any appreciable surface area has developed. The crystallite surface area is exposed on removal of material between the crystallites (1). One of the traditional activating agents for charcoal is chlorine, which presumably removes excess carbon as carbon tetrachloride. At the end of this process further activation produces no further increase in surface area and indeed may bring about a decrease by crystal growth. However, in our previous work (4) it was found possible to activate a porous but well-defined graphite and a non-porous carbon black by bromine sorption followed by high temperature treatment. It was therefore

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thought to be of interest to do similar work using as sorbents two highly activated charcoals. In addition it was hoped that such experiments would afford an opportunity to make an indirect measurement of the "density" of the sorbed bromine.

EXPERIMENTAL AND RESULTS

Two activated charcoals were chosen for this study. The first of these was a coconut shell charcoal some of whose properties have been given by McDermot and Arnell (3). The second was a charcoal manufactured by the Norit Co. and designated by them as Norit RG-1.

The nitrogen was supplied by the Canadian Liquid Air Co. and was stated to be 99.5% pure.

The experimental technique for bromination of the samples, removal of the bromine, and measurement of the low temperature nitrogen isotherms was similar to that already described (4). In one of the runs with Norit no attempt was made to remove the bromine. The freshly saturated sample was transferred to the sorption cell, cooled to 78° K., and evacuated to remove the air

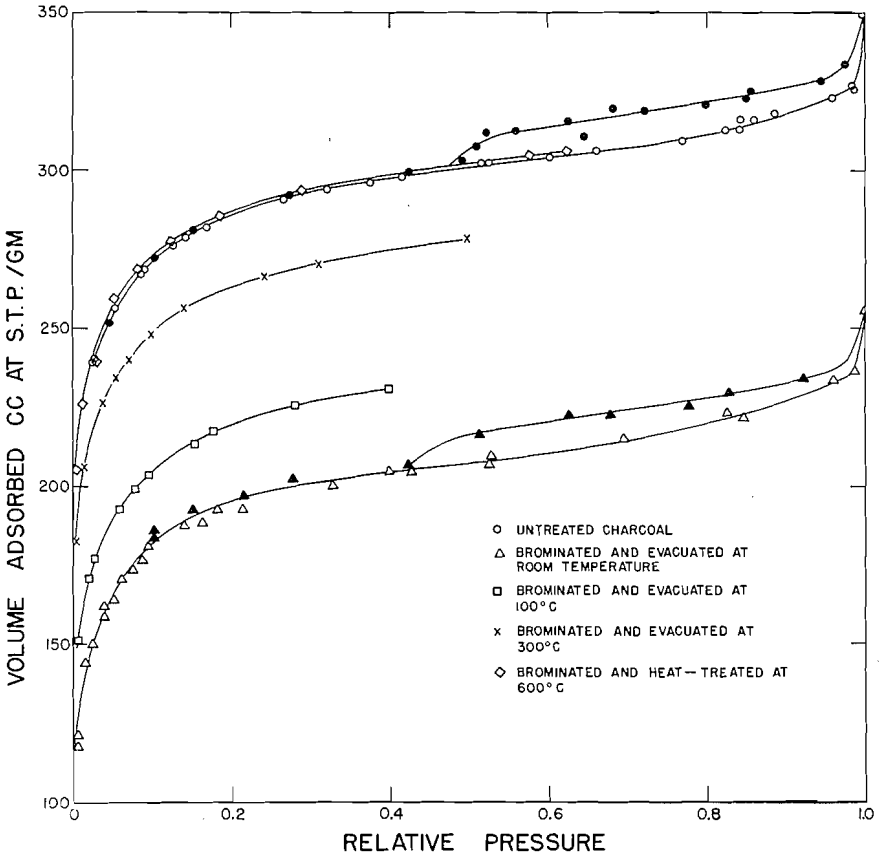

FIG. 1.

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in the cell. The only bromine lost was that which desorbed while the sample was being transferred to the sorption cell.

Fig. 1 presents some of the isotherms measured for nitrogen sorbed by the coconut shell charcoal and by a sample of the same charcoal which had been brominated and evacuated successively at room temperature, 100°, and 300° and heat-treated at 600° and 1000° C. It will be seen that the isotherm measured after the brominated charcoal was heated to 600° C. coincides with that of the untreated charcoal. The isotherm following the 1000° C. heating lies below that of the untreated charcoal. Fig. 2 shows the nitrogen isotherms for

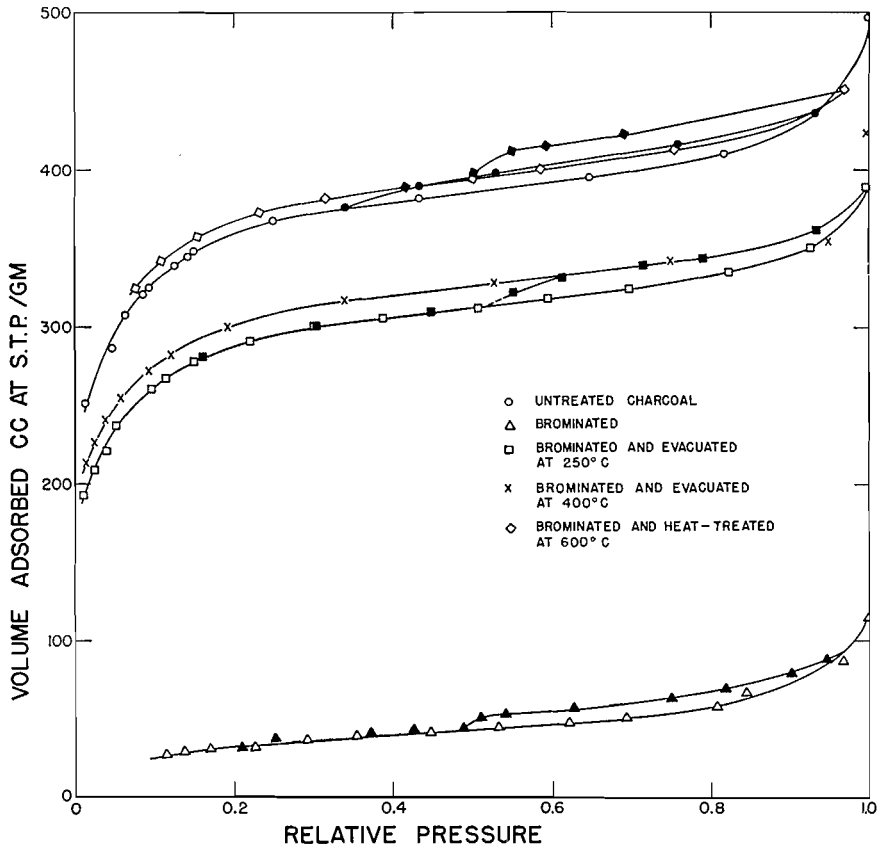

FIG. 2.

Norit RG-1 and for the same charcoal which had been brominated, evacuated at 250 and 400° C., and finally heat-treated at 600° C. It will be noted that the isotherm measured after treatment at 600° C. lies a little above that for the untreated charcoal.

Both charcoals were found to suffer net losses in weight as the result of the heat-treatments at 600° C. and 1000° C. These are given in Table I, which lists the original weights of the samples and the weights after heat-treatment at these temperatures.

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TABLE I

Treatment	Charcoal, gm.	
	Coconut shell	Norit
Original weight	0.536	1.084
Weight after the 600° treatment	0.528	0.971
Weight after the 1000° treatment	0.460	—

The losses in weight, which are as high as 12% of the original weight of the sample, are believed to be the result of combined losses of carbon and bromine, presumably in the form of carbon tetrabromide. It should be noted in this connection that the loss of carbon did not bring about any appreciable activation of either charcoal.

It was observed that, with the exception of the isotherm measured immediately after Norit was saturated with bromine, all of the isotherms were of exactly the same shape. It was found possible to make the isotherms of the brominated samples coincide approximately with that of the untreated sample by addition of constants to volumes adsorbed. The degree of coincidence is illustrated for the coconut shell and Norit charcoals by Figs. 3 and 4 respectively. In these calculations, the volumes of gas to be added to the isotherms of the brominated charcoals were chosen by making the isotherms coincide at $P/P_0 = 0.4$. The volumes so obtained, the quantities of bromine

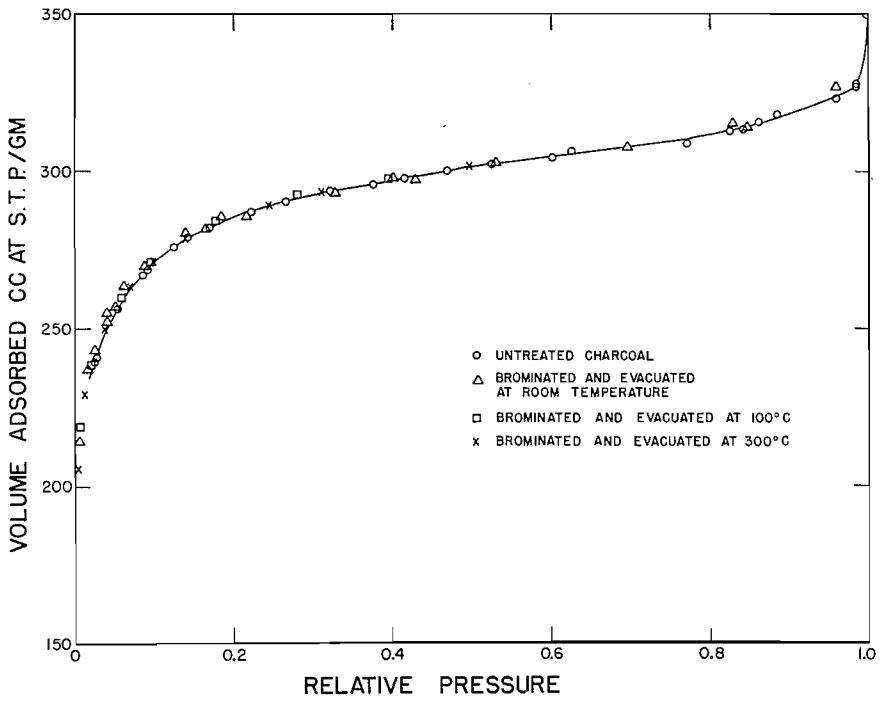

FIG. 3.

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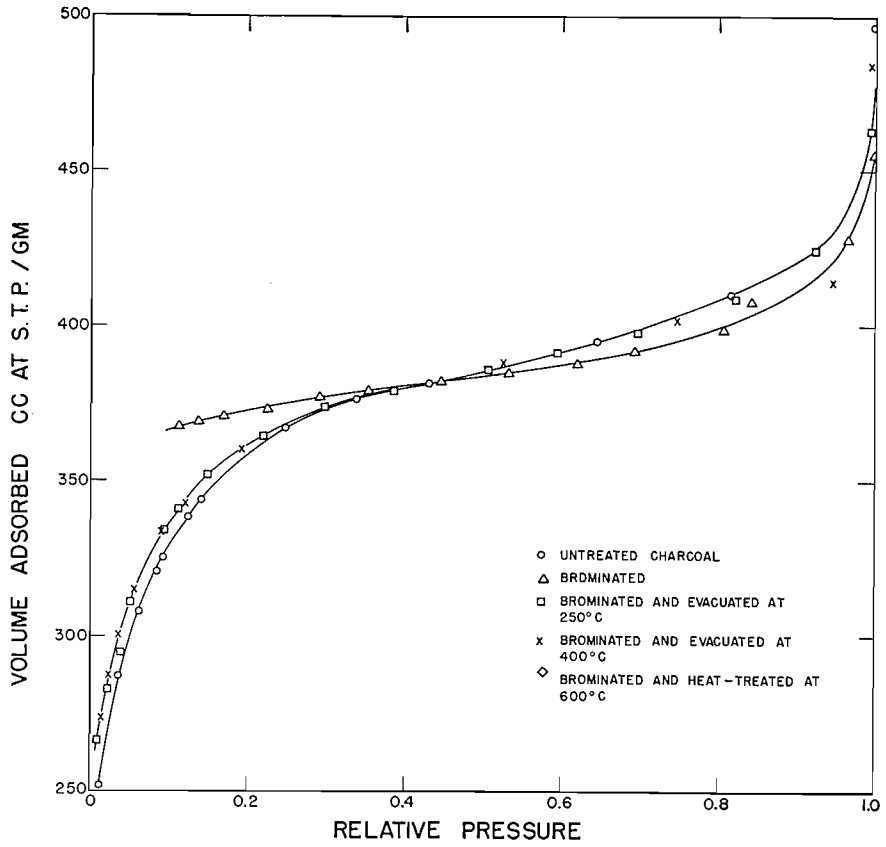

FIG. 4.

retained by the charcoals after each treatment, and the calculated values for the "density" of the adsorbed bromine are presented in Table II. It is assumed that since the upper parts of the isotherm coincide, the pores fill with liquid nitrogen to the same degree in both the treated and untreated samples. The volume of the sorbed bromine is then simply equal to the volume displacement required to make the isotherm of the brominated charcoal coincide with that of the untreated charcoal. It is further assumed that the sorbed nitrogen has the same density as that of the bulk liquid.

TABLE II

Charcoal	Treatment temperature, °C.	Volume of liquid N_2 added, cc.	Weight Br_2 sorbed, gm./gm.	"Density" of bromine, gm./cc.
Coconut shell	25	0.144	0.35	2.4
Coconut shell	100	0.104	0.23	2.2
Coconut shell	300	0.036	0.11	3.1
Norit	No evacuation	0.526	1.19	2.3
Norit	250	0.114	0.18	1.6
Norit	400	0.093	0.09	1.5

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DISCUSSION

The isotherms displayed in Figs. 1 and 2 demonstrate that no activation occurred when these brominated charcoals were heated to high temperatures. In fact the very opposite occurred in the coconut shell charcoal on bromination and heat-treatment at 1000° C. The absence of activation would appear to indicate that the charcoals underwent their maximum activation at the time of manufacture and that further efforts in this direction were useless and in one case caused sintering.

The "densities" given in Table II were calculated assuming that the sorbed liquid nitrogen has the same density as the bulk liquid. It would probably be more accurate to assume that the sorbed liquid nitrogen is somewhat less dense than the bulk liquid. McDermot and Tuck (5) have shown that water sorbed by charcoal is about 5% less dense than the bulk liquid. Since water and nitrogen molecules do not differ very much in size, it would be reasonable to suppose that sorbed liquid nitrogen was also about 95% as dense as the bulk liquid. The densities calculated on this assumption are given in Table III.

TABLE III

Charcoal	Treatment temperature, ° C.	Volume of liquid N_2 added, cc.	Weight Br_2 sorbed, gm./gm.	"Density" of bromine, gm./cc.
Coconut shell	25	0.152	0.35	2.3
Coconut shell	100	0.111	0.23	2.1
Coconut shell	300	0.038	0.11	2.9
Norit	No evacuation	0.560	1.19	2.1
Norit	250	0.121	0.18	1.5
Norit	400	0.099	0.09	1.4

It will be noted that they are somewhat lower (5 to 10%) than those listed in Table II. The density of solid bromine is 3.4 gm./cc. at its freezing point (2). The density at 78° K. is not available, nor are data available which allow for its calculation. However, it can be safely assumed that it is somewhat greater than the value 3.4 gm./cc. The values for the "density" of sorbed bromine which are listed in Tables II and III are all considerably lower than that of the bulk solid. McDermot and Tuck (5) postulated that water sorbed by charcoal was less dense than the bulk liquid because the water molecules packed less efficiently in pores of molecular dimensions than in bulk. It is suggested that this explanation also applies in the present case and that the much greater reduction in "density" of the sorbed bromine with respect to the bulk solid is due to the fact that bromine molecules are much larger than those of water. It will be noted that the "density" of the bromine sorbed by the Norit is less than that of the bromine sorbed by the coconut shell charcoal. The reason for this is thought to be that the Norit possesses smaller pores on the average than the coconut shell charcoal. Hence, the packing would be expected to be less efficient in the smaller pores than in the larger.

No attempt has been made to correlate the "density" of the sorbed bromine with the amount of bromine sorbed by the charcoals. It is considered that the "densities" are not sufficiently accurate for such a correlation.

ACKNOWLEDGMENT

The author would like to express his gratitude and thanks to Mr. A. Grey for his very competent assistance in carrying out the experimental work.

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ON THE STRUCTURE OF AGAR FROM GELIDIUM CARTILAGINIUM[1]

By A. N. O'Neill and D. K. R. Stewart

ABSTRACT

Agar from *Gelidium cartilaginium* has been analyzed for D-galactose, 3,6-anhydro-L-galactose, and sulphate. From these analyses and a study of the products of mercaptolysis it is suggested that agar from this source be represented as a chain of alternating D-galactose and 3,6-anhydro-L-galactose residues with a half-ester sulphate on about every 10th galactose unit.

Agar, a polysaccharide of certain red algae, has been known for many years, and its molecular structure has been extensively investigated (7, 13). However, no general agreement has been reached possibly because of the use of commercial preparations of uncertain origin and purity and the lack of a satisfactory analytical method for the determination of 3,6-anhydro-L-galactose. That this sugar is a component of agar has been recognized for some time (3, 5, 6, 10, 11), but the amount has been variously reported as from 7 to 18%. With D-galactose at 60% and sulphate at 1–5%, a considerable portion of this polysaccharide remains unidentified.

It is known that the D-galactose residues are joined through C_1 and C_3 in β-glycosidic linkages, and through the isolation and characterization of a disaccharide, 4-*O*-D-galactopyranosyl-3,6-anhydro-L-galactose, from an acid hydrolyzate of agar, Araki (1, 2) has shown that the 3,6-anhydro-L-galactose units are joined through C_4 to C_1 of a neighboring D-galactose residue.

Since agar appeared to have a structural resemblance to κ-carrageenin it was thought desirable to apply some of the methods developed during the investigation of the latter (8, 9) in an attempt to clarify some of the structural features of agar.

The polysaccharide was prepared from *Gelidium cartilaginium* and subjected to extensive purification. Galactose was determined after acid hydrolysis by quantitative paper chromatography. The 3,6-anhydro-L-galactose was estimated spectrophotometrically in the acid hydrolyzate as 5-hydroxymethyl-2-furaldehyde by the method described previously for κ-carrageenin (8, 12). The results are shown in Fig. 1. The following analyses for agar are averages of duplicate determinations: galactose, 53.5%; 3,6-anhydro-L-galactose, 38.1; sulphate, 4.1. The ratio of D-galactose to 3,6-anhydro-L-galactose residues is about 6: 5. This is the same ratio as was found for κ-carrageenin.

Samples of agar were suspended in aqueous sodium metaperiodate, and the periodate consumption was measured iodometrically. No reaction was demonstrable after 250 hr. so that no monosaccharide residue in agar contains contiguous hydroxyl groups.

After agar had been subjected to mercaptolysis as described previously for

[1]*Manuscript received August 13, 1956.*
Contribution from the National Research Council, Atlantic Regional Laboratory, Halifax, Canada. Issued as N.R.C. No. 4120.

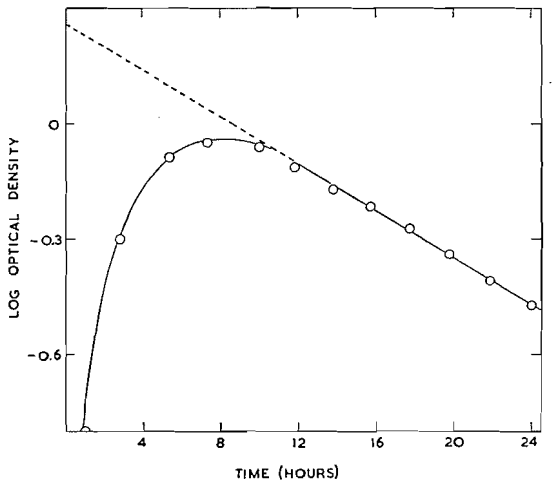

FIG. 1. The formation and decomposition of 5-hydroxymethyl-2-furaldehyde during the hydrolysis of agar in 1.25% concentration at 100° with 0.15 *N* sulphuric acid. Optical density was determined on a 1 → 250 dilution at 2850 Å.

κ-carrageenin the diethylmercaptals of D-galactose and 3,6-anhydro-L-galactose were isolated in almost equal yields. This confirms the work of Araki (4) on the exhaustive mercaptolysis of commercial agar. The material remaining after removal of these monosaccharide derivatives appeared, from paper chromatographic studies, to consist almost entirely of one disaccharide derivative. This has not yet been obtained in crystalline form.

The structures proposed previously for agar must therefore be revised, particularly with regard to the amount of the 3,6-anhydro-L-galactose component. With the exception of the number of half-ester sulphate residues it must be very similar to κ-carrageenin. If an unbranched chain is assumed, as is suggested from methylation, then the molecule of agar from *Gelidium cartilaginium* can be represented by a chain of alternate D-galactose and 3,6-anhydro-L-galactose residues with a half-ester sulphate on about every 10th galactose unit. The D-galactose residues are joined through C_1 to C_4 of neighboring 3,6-anhydro-L-galactose moieties and the latter through C_1 to C_3 of adjacent D-galactose residues. This disregards the presence of L-galactose but its amount, in any case, is very small ($< 1\%$) and it may well arise from a contaminating polysaccharide.

Such a structure is consistent with the instability of agar solutions to dilute acid. The 3,6-anhydro-L-galactose residues, which contain both a pyranose and a hydrofuranol ring, would be under considerable strain. The resulting highly strained glycosidic bonds involving C_1 of these residues would be expected to undergo rapid hydrolysis under relatively mild conditions. This would result in the formation of 3,6-anhydro-*aldehydo*-L-galactose, which in turn undergoes a series of dehydrations with ring rearrangement to give 5-hydroxymethyl-2-furaldehyde.

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EXPERIMENTAL

Preparation of Agar

Finely ground dry *Gelidium cartilaginium* (200 gm.) was extracted with 4 liters of water at 100° for two hours. The hot extract was filtered through muslin and centrifuged while still hot until a clear solution was obtained. This set to a stiff gel on cooling, was frozen overnight, and allowed to thaw on muslin whereby much of the water drained off. The gel was redissolved in 4 liters of water at 90° and the freezing and thawing repeated. The whole sequence was repeated an additional six times with the exception that the hot solution was centrifuged at 12,000 r.p.m. before freezing. The final gel was washed extensively with cold water, dehydrated with alcohol and acetone, washed with ether, and dried to yield 11 gm. of a fine white powder. Analyses: galactose, 53.5%; 3,6-anhydro-L-galactose, 38.1; sulphate, 4.1.

Mercaptolysis of Agar

Agar (5.3 gm.) was weighed into a three-necked flask fitted with a stirrer through a precision ground glass fitting and contained in an ice and water bath at 0°. Concentrated hydrochloric acid (70 ml.) at 0° was added slowly with stirring. When a thin slurry had been obtained ethyl mercaptan (30 ml.) was added dropwise and the mixture stirred at 0° for three hours. The temperature was increased to 14–15° and the stirring continued for 48 hr.

The resulting brown solution was poured with stirring into a suspension of 150 gm. of lead carbonate in 250 ml. of water at 0° and filtered. The filtrate and washings were saturated with hydrogen sulphide and the precipitate removed by filtration. The acidic solution so obtained was deionized by aeration with nitrogen in the presence of exchange resins Amberlites IR-100 and IR-4B.

D-*Galactose Diethyl Mercaptal*

The above neutral solution was concentrated under reduced pressure until crystallization commenced. After 24 hr. at 5° the crystalline material was recovered and the concentration repeated until no further crystalline material was obtained. In this manner 710 mgm. of D-galactose diethyl mercaptal was obtained, m.p. 142–143°, $[\alpha]_D^{25}$ −4.2° (*c* 1.0, water).

*3,6-Anhydro-*L*-galactose Diethyl Mercaptal*

The mother liquor obtained after crystallization of the D-galactose diethyl mercaptal was continuously extracted with ether for 24 hr. When the ether solution was cooled to 25° an additional 295 mgm. of D-galactose diethyl mercaptal was obtained. Concentration of the ether solution to a small volume and cooling to 5° yielded 1.04 gm. of crystalline 3,6-anhydro-L-galactose diethyl mercaptal, m.p. 111–112°, $[\alpha]_D^{25}$ +10° (*c* 1.0, water).

The Residual Mercaptolyzate

The aqueous solution remaining after the extraction with ether was concentrated under reduced pressure to a thick sirup which was further dried by the distillation of added ethanol, yield 2.3 gm. All attempts to crystallize this material failed. Paper chromatographic studies indicated essentially a single

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component which moved at about the same rate as 4-*O*-β-D-galactopyranosyl-3,6-anhydro-D-galactose diethyl mercaptal (9). Acetylation of the sirup with pyridine and acetic anhydride in the usual manner yielded 3.5 gm. of acetate, which has also resisted crystallization.

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THE BIOGENESIS OF ALKALOIDS

XVII. FURTHER STUDY OF THE ROLE OF ORNITHINE IN THE BIOGENESIS OF STACHYDRINE[1]

By Arthur Morgan[2] and Léo Marion

ABSTRACT

Earlier attempts to feed ornithine-2-C^{14} to *Medicago sativa* L. Grimm had failed to produce any labelled stachydrine. Repetition of the work has confirmed this result, and a study of the amino acids present in the plant has shown that the proline also was inactive. Feeding pyridoxine with ornithine-2-C^{14} to the plant did not produce active stachydrine, but gave rise to radioactive proline. Of the other amino acids present, glycine, aspartic acid, and glutamic acid were also active. A similar feeding experiment with radioactive ornithine and pyridoxine, using older plants, also failed to produce active stachydrine although, as before, the proline was active and so was the keto acids fraction.

The results seem to indicate that ornithine may be the precursor of stachydrine, but that the transformation to proline and the methylation to the alkaloid occur at a later stage of growth, possibly at seed formation.

In a recent study of the role of ornithine in the biogenesis of stachydrine, Leete, Marion, and Spenser (6) administered ornithine-2-C^{14} to two-week-old alfalfa seedlings (*Medicago sativa* L. Grimm), and after 10 days harvested the plants and isolated the stachydrine, which, however, was not active. This could have been due to one of two reasons, i.e., that the synthesis of stachydrine might occur at a later stage in the plant's development, in which case the isolated material would have been translocated from the seeds, or that ornithine might not be the precursor of stachydrine in alfalfa.

It was decided to investigate the metabolism of ornithine in this plant with particular reference to the other amino acids. Vickery (10, 11) has shown that alfalfa contains lysine, arginine, asparagine, and tyrosine. Two-dimensional paper chromatography has now revealed the following additional amino acids: alanine, aspartic acid, glutamic acid, glycine, isoleucine, leucine, phenylalanine, proline, serine, threonine, and valine.

In a first experiment, alfalfa was grown under the same conditions as previously described (6) except that the plants were harvested on the 19th day, after 14 days in contact with ornithine-2-C^{14}. The plants were extracted as before (6) and the protein-free extract was divided into two portions. The larger (85%) was used for the isolation of stachydrine, which was found to be inactive, thus confirming the previously reported findings (6). The smaller portion was evaporated to dryness, the residue dissolved in 0.5 *N* acetic acid, chromatographed on Dowex 1-X8, and eluted as described by Hirs, Moore, and Stein (5). This treatment permitted the isolation of glutamic and aspartic acids and gave a forerun which on further chromatography on Dowex-X4 yielded the neutral and basic amino acids. Glutamic acid and aspartic acid

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Contribution from the Division of Pure Chemistry, National Research Council, Ottawa, Canada. Issued as N.R.C. No. 4121.
[2]*Postdoctorate Fellow of the National Research Council of Canada.*

were found to be radioactive as well as ornithine and glycine. The proline was inactive.

It is obvious that at least up to 19 days of growth the plant is incapable of converting ornithine into either stachydrine or proline. If the plant synthesizes the alkaloid at a later stage of growth only, it was thought that a substance like pyridoxine known to catalyze many reactions of amino acids might induce the plant to produce the pyrrolidine ring.

In a further experiment, pyridoxine in a concentration of 4×10^{-6} *M* (1) was added to the nutrient solution fed to alfalfa seedlings growing in contact with ornithine-2-C^{14}. After harvesting, the plant was extracted as before and the free amino acids and the stachydrine were isolated. The stachydrine was inactive, but there was appreciable activity in the proline. Glutamic and aspartic acids, which in this case were not completely separated, were also active and, although an accurate assay was not possible, it appeared that the former was the more active.

It was hoped that older plants might be able to utilize the active proline produced in the plant from labelled ornithine under the influence of pyridoxine. Thirty-six 12-week-old alfalfa plants grown in soil were therefore transferred to hydroponic solutions containing ornithine-2-C^{14} and pyridoxine in the same concentration as before and were grown for three days, the roots being kept in darkness. After this time the leaves showed appreciable activity, so that the plants were harvested and the roots separated from the aerial portions of the plants. Each part was worked up separately for alkaloids and it was found that the aerial parts contained much more stachydrine than the roots. After recrystallization, however, the stachydrine was found in both cases to be inactive. Analysis of a mixture of root and aerial extracts showed that as before, the glutamic acid, aspartic acid, and proline contained most of the activity present in the free amino acids. The keto acids isolated by the method of Virtanen (12) were also fairly active.

EXPERIMENTAL

Feeding and Extraction of 19-day Alfalfa

Alfalfa seeds (20 gm.) were dusted with the fungicide Semesan and spread evenly on top of a double layer of wetted Whatman's No. 1 filter paper in two glass trays. These were kept in a germinating cabinet for one week, the only addition being distilled water. After this period they were brought into the open and fed with ornithine-2-C^{14} (13.36 mgm., with a specific activity of 4.81×10^{7} disintegrations per minute per millimole, and a total activity of 3.87×10^{6} d.p.m.) dissolved in water (20 ml.). After 12 days the plants were extracted with boiling water as previously described (6). The extract contained 21% of the activity administered to the plants. The protein was precipitated with lead acetate and filtered off. The excess lead was removed with hydrogen sulphide and the filtrate concentrated to 100 ml.

A portion (85 ml.) of this solution was evaporated to dryness and the residue (3.6 gm.) worked up as usual for stachydrine and choline by means of the reinecke salts. For an initial purification the reineckates were dissolved in

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acetone (10 ml.), chromatographed on alumina, and eluted with acetone. Evaporation of the eluate gave a pink crystalline mass (0.56 gm.) of mixed stachydrine and choline reineckates which were separated as previously described (6) and converted to the chlorides.

The remaining 15 ml. of plant extract was evaporated to dryness and dissolved in 0.5 *M* acetic acid (5 ml.). A column of Dowex 1-X8 ion exchange resin (33×2.1 cm.) was prepared according to Hirs, Moore, and Stein (5) and percolated for 24 hr. with 0.5 *M* acetic acid. The solution was added and the material eluted with 0.5 *M* acetic acid at a flow rate of 35 ml. per hour. Fractions were collected at 12 min. intervals and a sample (0.25 ml.) from every alternate fraction was analyzed by paper chromatography. The dried samples were dissolved in methanol (0.05 ml.), spotted on Whatman's No. 1 filter paper, and chromatographed unidirectionally in propionic acid – methyl ethyl ketone – water (25: 75: 30) (2). The results are given in Table I.

TABLE I

FRACTIONS FROM DOWEX 1-X8 COLUMN

Fractions No.	Substance	Wt. in mgm.	Specific activity*
9–15	Neutral and basic amino acids, keto acids, etc.	582	—
27–39	Glutamic acid	66	1.11×10^4
65–80	Aspartic acid	50	0.89×10^4

**Specific activity is given in disintegrations per minute per millimole.*

Fractions 9 to 15 were combined and evaporated to dryness and the residue dissolved in *N* hydrochloric acid (5 ml.). Dowex 50-X4 ion exchange resin was prepared as described by Moore and Stein (7), slurried in 2 *N* hydrochloric acid, and poured to form a column (60×2.1 cm.). The column was washed with *N* hydrochloric acid for 12 hr. before the solution was added. Elution was done with hydrochloric acid at a rate of flow of 45 ml. per hour and fractions were collected every 12 min. The hydrochloric acid used for elution was normal at the beginning but the concentration was gradually increased to 4 *N*. Samples from every alternate tube were analyzed as above and the results are given in Table II.

Feeding and Extraction of 12-week-old Alfalfa

Thirty-six 12-week-old alfalfa plants which had been grown in soil were washed well with water, and each plant was supported with the roots in a beaker containing aerated nutrient solution (200 ml.) (3) to which pyridoxine had been added at a concentration of 4×10^{-6} *M* (1). The roots were kept in darkness. After one day, ornithine-2-C^{14} (60.2 mgm., specific activity 4.81×10^7 d.p.m. per millimole or total activity 1.74×10^7 d.p.m.) in water (50 ml.) was distributed equally between the 36 plants. After three days, activity was detectable in the leaves and the plants were harvested. The aerial parts (41.5 gm.) were separated from the roots (20 gm.) and after being washed, each portion was extracted separately by the same procedure as before. The roots

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TABLE II

CHROMATOGRAM ON DOWEX 50-X4

Fractions No.	Substance	Wt. in mgm.	Specific activity*
55–79	Serine	10	—
81–87	Threonine	10	—
97–117	Glycine	22	0.33×10^4
118–137	Alanine	40	
155–175	Valine	60	
183–193	Proline	40	
201–209	Methionine	18	
249–267	Isoleucine	95	
269–289	Leucine	44	
351–371	Ornithine	40	5.5×10^4

**Specific activity given in disintegrations per minute per millimole.*

(activity 6.57×10^5 d.p.m.) were much more active than the aerial portion (activity 1.22×10^5 d.p.m.) probably owing to some adsorbed ornithine not completely removed by washing with water. After precipitation of the protein as described above, aliquots (65%) of each extract were used for the isolation of stachydrine. The stachydrine content of the aerial portion (97 mgm.) was much greater than that of the roots (16.7 mgm.). In both cases the alkaloid was inactive.

The remaining portions of the two extracts were combined and analyzed for amino acids exactly as before on a Dowex 1-X8 column. The basic and neutral amino acids plus keto acids weighed 1196 mgm. The isolated glutamic acid, 45 mgm., had a specific activity of 1.64×10^4 d.p.m. per millimole, and the aspartic acid, 23 mgm., had a specific activity of 1.58×10^4 d.p.m. per millimole.

The neutral and basic amino acids and keto acids were separated on Dowex 50-X4 as before. The proline fraction contained 10.6% of the total activity applied to the column (6.04×10^4 d.p.m.) and had a specific activity of 4.84×10^3 d.p.m. per millimole. The forerun from the column contained the plant acids and keto acids, which accounted for 21% of the total activity of the chromatogram. The 2,4-dinitrophenylhydrazones of the keto acids isolated and purified by the method of Virtanen (12) had about 30% of the activity of the forerun.

DISCUSSION

The present experiments show that under the conditions used by Leete, Marion, and Spenser (6), the metabolic pathway ornithine→proline is blocked. The principal pathway by which proline is synthesized in animal tissues (8, 9) and in molds (4) is from glutamic acid through the semialdehyde and pyrroline carboxylic acid, and in these systems glutamic acid is also the precursor of ornithine. Since in alfalfa ornithine is converted to glutamic acid it must be concluded, provided the biogenetic pathway be the same, that the block is between glutamic acid and proline.

When both pyridoxine and ornithine-2-C^{14} were added to the nutrient solution, the glutamic acid as well as proline was radioactive although the

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stachydrine was again inert. The specific activity of the glutamic acid was higher than that of the proline, and this suggests that the former may have been the precursor of proline.

Assuming that stachydrine is produced in the plant from proline by methylation, it seems legitimate to conclude that up to 12 weeks the alkaloid is not being synthesized in alfalfa. Even in the presence of pyridoxine, the proline→stachydrine pathway is still blocked, i.e., methylation does not take place. Since stachydrine is stored in the seeds it may be assumed that it is synthesized only during the late flowering stages, at the period of seed formation. Experiments are underway in which it is hoped to induce methylation to take place at an earlier period of growth.

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THE GAS PHASE PHOTOLYSIS OF ACETIC AND PROPIONIC ANHYDRIDE[1]

By P. Ausloos[2]

ABSTRACT

The photolysis of acetic anhydride has been reinvestigated in the temperature region from 30 to 195° C. Two primary processes occur with about equal probability:

$$(CH_3CO)_2O + h\nu = CH_3COO + CH_3CO,$$

$$(CH_3CO)_2O + h\nu = CH_2CO + CH_3COOH.$$

Analogous primary processes have been proposed for the photochemical decomposition of propionic anhydride.

The abstraction reaction:

$$CH_3 + (CH_3CO)_2O = CH_4 + CH_3COCOOCH_2$$

is of importance, and the results indicate that it has an activation energy of about 9.6 kcal./mole.

EXPERIMENTAL

Acetic and propionic anhydride were obtained from the Eastman Kodak Company (White Label) and thoroughly outgassed in the vacuum line.

The light source used in all experiments was a Hanovia (16A-13) SH type medium pressure lamp. The intensity was varied by means of gratings; no other filters were used in this work.

The gas phase photolysis was carried out in a cylindrical quartz cell about 10 cm. long (180 cm.^{3}). Pressures were measured by means of a U-tube mercury manometer which also served to isolate the cell from the remainder of the apparatus. Since the vapor pressure of acetic anhydride was only about 0.6 cm. at 25° C., the external parts of the reaction system were electrically heated.

The analysis system consisted of three traps, a low temperature fractionating column, McLeod gauge, Toepler pump, and gas burette.

In the course of an analysis the CO–CH_4 fraction was removed at liquid nitrogen temperature and passed over hot (240° C.) copper oxide. The C_2 fraction was taken off at −170° C. C_2H_4 was determined by hydrogenation over a Ni catalyst (8). A fraction coming over at −140° C. was on a few occasions analyzed by a mass spectrometer and consisted mainly of CO_2 and CH_2CO. It was found possible to determine ketene by bringing the fraction over a Ni catalyst (150° C.) in the presence of hydrogen. While carbon dioxide did not react, ketene broke down to methane, carbon monoxide, and small quantities of ethane. The amount of carbon dioxide originally present could be determined by bringing the whole mixture over ascarite. CH_3CHCO was determined by bringing the C_4H_{10}–CH_3CHCO fraction, removed at −110° C., over ascarite. The amount of conversion of acetic and propionic anhydride was kept below 5%.

[1]*Manuscript received August 16, 1956.*
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RESULTS AND DISCUSSION

Acetic Anhydride

Table I includes the results of runs conducted in the gas phase at temperatures ranging from 30 to 195° C. The rates quoted are in the units cc. at NTP per min. Experiments 1 to 5 were performed at approximately constant incident light intensity and constant pressure. In the first three runs, the methane concentration was too small to be measured accurately. Although there is some scattering of the results, it can be seen that the ketene and carbon dioxide concentrations are independent of temperature, while the rate of the carbon monoxide and ethane production decreases sharply in the lower temperature region. These results can be accounted for by postulating that two primary processes occur with about equal probability:

TABLE I

GAS PHASE PHOTOLYSIS OF ACETIC ANHYDRIDE

Run	Temp., °C.	Pressure, cm.	Rate, cc./min. $\times 10^4$					$R_M/R_E^{1/2} \times 10^{13}$, cm.$^{3/2}$ molecule$^{-1/2}$ sec.$^{-1/2}$	$(C_2H_6+\frac{1}{2}CH_4)/CO$
			CO	CO_2	CH_2CO	C_2H_6	CH_4		
1	30	0.68	5.30	21.0	19.2	7.80			
2	63	0.67	10.3	22.3	22.0	11.0			
3	93	0.72	14.0	21.6	21.4	15.1			
4	139	0.75	21.8	22.0	21.3	22.2	0.76		
5	165	0.73	23.0	24.5	22.1	18.6	1.40		
6	107	3.75	58.0	60.0	55.0	57.0	2.30	1.54	1.001
7	125	4.20	64.0	66.0	63.0	62.5	4.55	2.80	1.02
8	126	4.20	9.50	9.45	8.95	7.61	1.74	3.05	0.89
9	143	4.25	70.5	71.0	68.2	64.0	7.80	4.87	0.96
10	165	4.30	92.0	97.0	96.5	85.0	13.8	7.82	0.995
11	166	4.30	11.2	12.0	11.0	7.05	4.08	8.00	0.812
12	165	4.30	1.51	1.40	1.20	0.51	1.11	8.15	0.71
13	196	5.00	97.5	96.8	280.0	48.7	24.6	17.1	0.626

$$(CH_3CO)_2O + h\nu = CH_3COO + CH_3CO, \qquad [Ia]$$

$$(CH_3CO)_2O + h\nu = CH_2CO + CH_3COOH. \qquad [IIa]$$

It is known (2, 7) that in the gas phase, for comparable systems, the CH_3COO radicals decompose easily at low temperature. This explains the constancy of the CO_2 concentration over the whole temperature region. The decrease of the CO concentration with decrease in temperature is due to the higher stability of CH_3CO at low temperatures. The fact that at these temperatures the C_2H_6 concentration is larger than the CO concentration indicates that some biacetyl is formed by the recombination of two acetyl radicals. At higher temperatures the CO concentration is equal to the CO_2 concentration as it should be if [I*a*] and [II*a*] were the only two primary processes occurring.

From these results it is not possible to decide if the process

$$(CH_3CO)_2O + h\nu = CH_3COCOO + CH_3 \qquad [III]$$

followed by the thermal decomposition of CH_3COCOO into CH_3CO and CO_2 is of any importance. Analogy with the photochemical decomposition of simple alkyl esters (2) favors, however, process [I*a*].

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In a recent publication (4) on the photochemical decomposition of acetic anhydride, no ketene was observed. Instead, a value of about two was found for the ratio CO_2/CO. This can be explained by the fact that the CH_2CO–CO_2 fraction was brought over ascarite, which absorbs both compounds. This procedure led the authors to the erroneous conclusion that the fraction consisted entirely of CO_2.

Incidentally, it may be mentioned that runs done at high conversion (results not included in this paper) always lead to much higher values for the CO/CH_2CO ratio, while at the same time increasing amounts of ethylene are found in the C_2 fraction. This can be accounted for by the photochemical decomposition of ketene, which is of importance at higher conversions.

For runs performed at temperatures above 170° C. large quantities of ketene were detected. Run 13 at 196° C. is given as an example in Table I. There is no doubt that the excess ketene is formed by the thermal decomposition of acetic anhydride. A few dark runs performed at temperatures up to 300° C. showed no evidence of any radicals formed during the thermal decomposition, while the only gaseous product found was ketene. This is in accordance with the findings of Szwarc and Murawski (9), who studied the pyrolysis of acetic anhydride by the toluene carrier technique and concluded that the decomposition occurs by a molecular rearrangement:

$$(CH_3CO)_2O = CH_2CO + CH_3COOH, \qquad E = 34.5 \text{ kcal./mole.}$$

In order to obtain information about the formation of CH_4 and C_2H_6, a few runs (6 to 13) were performed at higher pressures and varying intensities. If both compounds are only formed by reactions 1 and 2,

$$CH_3 + (CH_3CO)_2O = CH_4 + CH_3COCOOCH_2, \qquad [1]$$

$$CH_3 + CH_3 = C_2H_6, \qquad [2]$$

the following relationship exists:

$$k_1/k_2^{\frac{1}{2}} = R_M/R_E^{\frac{1}{2}}\,(A)\,.$$

R_M and R_E represent respectively the rate of formation of methane and ethane. (A) indicates the concentration of acetic anhydride.

Values of $R_M/R_E^{\frac{1}{2}}$ (A) are given in Table I. Runs 10, 11, and 12 indicate that a 70-fold variation of the intensity affects this ratio only to a small extent. This may be considered as evidence for the fact that CH_4 and C_2H_6 are only produced by reactions 1 and 2. In Fig. 1, $k_1/k_2^{\frac{1}{2}}$ has been plotted against $1/T$. A value of 9.6 kcal./mole can be obtained from the slope of the Arrhenius plot. This value is comparable to the activation energy found for the abstraction of a H-atom from acetone, although the steric factor is about two times lower.

The values of $(\frac{1}{2}CH_4 + C_2H_6)/CO$ for the high pressure runs have been given in the last column of Table I. This ratio should be equal to one if the CH_3 radicals are only consumed by reactions 1 and 2. Values close to one were obtained for the high intensity runs 6, 7, 9, and 10, while lower values were found for the other runs. This is mainly due to the photochemical decomposition of ketene and the occurrence of the recombination reaction:

$$CH_3 + CH_3COCOOH_2 = CH_3COCOOC_2H_5.$$

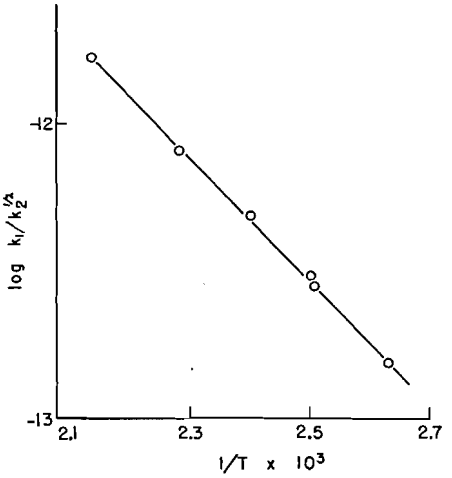

FIG. 1.

Propionic Anhydride

For comparison, the photochemical decomposition of propionic anhydride has been investigated very briefly. The average values for the rates of the reaction products of three runs performed at 115° C., 1.55 cm. pressure, and constant intensity are given in Table II.

TABLE II

GAS PHASE PHOTOLYSIS OF PROPIONIC ANHYDRIDE (RATE, CC./MIN. $\times 10^4$)
Temp., 115° C. Pressure, 1.55 cm.

CO	24.0	C_2H_4	2.8	CH_3CHCO	17.6
CO_2	23.8	C_2H_6	6.5	C_4H_{10}	17.0

These results point to primary processes analogous to those proposed for acetic anhydride:

$$(C_2H_5CO)_2O + h\nu = C_2H_5CO + C_2H_5COO, \qquad [Ib]$$

$$(C_2H_5CO)_2O + h\nu = CH_3CHO + C_2H_5COOH. \qquad [IIb]$$

The fact that the CO and CO_2 rates are equal indicates that under these conditions C_2H_5CO and C_2H_5COO are entirely decomposed. Ethylene and butane are mainly produced by the disproportionation and combination of the ethyl radicals.

CONCLUSION

Primary processes [II*a*] and [II*b*] as well as the thermal decomposition of acetic and propionic anhydride probably involve a "cyclic hydrogen bridge" as proposed for the thermal decomposition of esters (6). Pyrolysis studies of esters with a β-hydrogen in the alkyl group (1, 3) have indeed shown that these compounds decompose into the corresponding acid and alkene. Recently (2) it has been found that absorption of a photon by these molecules may also lead to a direct decomposition into an acid and an alkene.

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The thermal and photochemical decomposition of certain molecules following the same pattern can be explained (5) by considering the primary process as an internal conversion directly followed by a molecular elimination. This internal conversion probably produces a "hot" molecule in the electronic ground state, which may be expected to behave like a normal thermally excited molecule.

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SOLVOLYSIS IN DEUTERIUM AND HYDROGEN OXIDE[1]

By P. M. Laughton and R. E. Robertson

ABSTRACT

Rate data for a series of benzenesulphonates, halides, and methyl methanesulphonate were determined in light and heavy water. The rate ratio k_{D_2O}/k_{H_2O} varied with the nature of the anion being formed from 0.94 for the hydrolysis of methyl methanesulphonate to 0.78 for methyl chloride. This difference in ratio was attributed to differences in the nature of the solvation of the initial states. No appreciable differences arose, however, through the alkyl series methyl, ethyl, isopropyl benzenesulphonates, and the difference for the ratio k_{D_2O}/k_{H_2O} between MeCl and *t*-butyl chloride was small, contrary to recently published work.

In this paper we compare the relative rate data for the solvolysis of several alkyl halides and sulphonates in light and heavy water.

Recent work reported by this laboratory (3) has been particularly concerned with the role of the solvent in solvolytic reactions, and some measure of success has been achieved in correlating the changes in the derived activation energies with two properties, namely: the dielectric constant and the molecular volume of the hydroxylic solvent. When this correlation was extended to alcohol–water mixtures (4), a discontinuity was observed in the region of 0.1 mole fraction of alcohol. This behavior was attributed to the occurrence of a relatively rapid breakdown in the quasi-crystalline water structure resulting in lower activation energies. We were accordingly led to seek further evidence for the effect of structure on the rates of solvolysis by a comparison of the ratio k_{D_2O}/k_{H_2O} for a series of benzenesulphonates, since it is known that heavy water has more structure than light water (15) while the parameters (5) of the correlation remain relatively constant (ϵ H_2O: 78.25, D_2O: 78.54, with a maximum 0.35% difference in molar volume).

The appearance of a paper by Swain, Cardinaud, and Ketley (13) dealing with solvolytic rate ratios in light and heavy water led to an extension of the original study to include a number of halides, since the conclusions reached by the above-mentioned authors were at variance with our own.

Although Olivier (8), in the only simple solvolysis previously studied in both waters, reported a 16% reduction in rate of hydrolysis of *n*-hexyl bromide in heavy water, Swain and co-workers found no difference for k_{D_2O}/k_{H_2O} for methyl chloride and iodide within experimental error. This was surprising not only when compared with the results of Olivier but also because our own work on benzenesulphonates had shown a decrease. Moreover, they reported an unexpectedly large difference in the rate ratio between methyl chloride (1.0 ± 0.1) and *t*-butyl chloride (1.4 ± 0.1). This difference was attributed to the greater electrophilicity of light water toward chlorine, an interpretation which seemed to us to be much oversimplified.

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EXPERIMENTAL

Materials

The benzenesulphonic esters have been previously described (9).

Methyl bromide and methyl chloride were from Matheson lecture bottles. Mass spectrometric examination of the bromide failed to disclose any contaminant. The tertiary butyl chloride was the middle cut of Eastman Kodak white label material distilled with negligible change in boiling point or refractive index through a long Vigreaux column. The benzyl bromide was Eastman Kodak white label grade and was used without further purification.

The purity of each substance with respect to alternate reactants was confirmed by the excellent linearity of all the rate plots.

The samples of heavy water used were obtained from Atomic Energy of Canada Limited, and were in the range 99.8 to 99.9% D_2O as supplied. A number of runs were carried out in each sample by redistillation, the alcohol-containing foreruns being rejected. Anhydrous sodium carbonate was used to destroy any volatile acids.

Method

The conductance method used and the method of calculation have been described previously (10).

In most cases, the substrates were dissolved in deaerated solvent to give stock solutions. The cells were conventional in the use of shiny platinum electrodes in a vertical arrangement.

Methyl chloride was introduced by bubbling the gas through a reservoir immersed in the bath and attached to the cell by 20 cm. of 1 mm. capillary. A similar cell was used for *t*-butyl chloride.

While no attempt was made to measure the rates at exactly the same concentration, the presence of perceptible ionic strength effects with methyl bromide confirmed the necessity of operating at low concentration (0.0005–0.002 *M*) and over approximately the same range in comparative runs.

DISCUSSION

The experimental data are summarized in Tables I and II. Two aspects of these data particularly invite explanation. One is the variation of the ratio

TABLE I

SOLVOLYTIC RATE CONSTANTS FOR THE REACTION OF SOLUTES IN HYDROGEN AND DEUTERIUM OXIDE

Solute	*T*, °C.	$k_{H_2O}\times10^5$ sec.$^{-1}$	$k_{D_2O}\times10^5$ sec.$^{-1}$	k_{D_2O}/k_{H_2O}
MeCl	89.957	5.64±0.2*	4.381±0.007	0.780
t-BuCl	4.003	136.7 ±0.7	95.0 ±0.8	0.695
	14.031	636 ±3	473 ±3	0.744
MeBr	70.498	10.65±0.04	8.55 ±0.03	0.803
	80.003	27.13±0.02	21.99 ±0.04	0.810
	89.947	67.0 ±0.2	54.8 ±0.1	0.818
i-PrBr	50.001	11.29±0.03	8.84 ±0.08	0.780
$PhCH_2Br$	29.997	27.61±0.08	20.33 ±0.14	0.735
MeO_3SMe	59.996	22.03±0.04	20.64 ±0.08	0.937

**Average deviations from the mean.*

TABLE II

SOLVOLYTIC RATE CONSTANTS FOR A SERIES OF BENZENESULPHONIC ESTERS IN HYDROGEN AND DEUTERIUM OXIDE

R	T, °C.	$k_{H_2O} \times 10^5$ sec.$^{-1}$	$k_{D_2O} \times 10^5$ sec.$^{-1}$	k_{D_2O}/k_{H_2O}
Me	39.854	(6.674)*	6.048±0.012	0.906
	49.970	(19.59)	17.60 ±0.03	0.898
	60.622	(55.92)	50.62 ±0.11	0.905
	70.258	(132.7)	120.8 ±0.2	0.910
Et	49.984	(13.39)	16.74 ±0.06	0.911
	60.627	(54.12)	49.5 ±0.5	0.915
	70.258	(133.3)	120.3 ±0.4	0.902
i-Pr	7.513	(6.022)	5.52 ±0.03	0.917
	15.000	(17.54)		
		17.52±.02	16.10 ±0.04	0.918
	30.103	(124.3)		
		124.9	114.9 ±0.3	0.924

**Bracketed values were calculated from three-constant equations (11).*

k_{D_2O}/k_{H_2O} with the nature of the anion being created in the transition state. The second relates to the effect on the rate ratio of a probable change along the reaction parameter resulting from a change in the alkyl group (3).

We do not have sufficient data to make an exact estimate of the differences in the entropies and heats of activation between the two solvents, but enough exists to show that the rate reductions in heavy water arise almost entirely from the lower entropies of activation. The constancy in the rate ratios over a series of temperatures indicates that the differences in the heats and in the heat capacities of activation between the two media are negligible, though the temperature range may not be large enough to make this conclusion significant in the case of the latter. According to Wirtz (15) the structure of D_2O at temperature T resembles that of H_2O at a lower temperature $(T-\Delta T)$. This ΔT is roughly constant with temperature.

Variation in the Ratio with the Anion

A rather simple explanation has occurred to us for the variation in k_{D_2O}/k_{H_2O} according to the order $MeO_3SMe > MeO_3SPh > MeBr > MeCl$. This explanation is based on a consideration of differences involving both the initial and transition states. Although we lack initial state data such as heats of solution for all of the respective esters, certain qualitative distinctions may be noted. Thus the sulphonic esters are more soluble in water than are halides of comparable size or molecular weight. Such an enhancement of solubility must arise from stronger solvent–solute interaction, presumably hydrogen bonding. It cannot arise from decreased solute–solute interaction since the benzenesulphonates appear to have smaller vapor pressures than the bromides of comparable molecular weight (b.p. of $C_6H_6CH_2Br$: 80°C. at 10 mm., mol. wt. 171; of $C_6H_6SO_3CH_3$: 140°C. at 8 mm., mol. wt. 172). Since the decrease in the rate of solvolysis in heavy water may be attributed to the necessity of breaking up a more stable solvation shell ("iceberg") surrounding the initial state (1) to achieve a transition state which is similar for both light and heavy water, any special interaction in the initial state will tend to

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decrease the difference between the initial and transition states and hence between the two media. On the basis of the solubility differences noted above, we expect such solute–solvent interaction in the initial state to be greater for the sulphonates than for the halides, and to be greater for the methanesulphonate than for the benzenesulphonate as a result of the greater shielding effect of benzene ring. If we may assume that other factors, including differences in the transition state, contribute less than the initial state difference, the above argument provides a qualitative basis for understanding the trend in k_{D_2O}/k_{H_2O} values for the anions here treated.

Other factors of lesser importance probably contribute to the observed ratios. Chloride ion has been reported (6) to have a lower heat of solution (by 0.13 kcal./gm. ion) in heavy water than in light water. No comparable data for the sulphonates are available. Schwarzenbach (12) has shown that heavy water is less basic than light water, but this does not necessarily imply a corresponding difference in nucleophilicity. Also, nucleophilicity probably plays a minor role in solvolysis in water, especially for the sulphonates.

No substantial part of the ratio k_{D_2O}/k_{H_2O} can derive from a medium effect since the ratio for methyl methanesulphonate is so close to unity. In any case, the small differences in dielectric constant and molar volume between the two media would not lead one to predict more than a small effect from such a source, despite Schwarzenbach's guess (12) of about 5% based on equilibria in aqueous alcoholic mixtures.

Variation of the Alkyl Group

Swain and co-workers (13) reported a relatively large difference between the ratio k_{D_2O}/k_{H_2O} for methyl chloride and *t*-butyl chloride. They attributed the difference to the increased electrophilic solvation of the forming chloride ion in the more ionic S_N1 transition state of the latter.

We tend to discount this explanation for two reasons. First, our own data (Table II) largely eliminates the difference. In fact, the differences introduced in several systems as a result of changes in the alkyl group are surprisingly small. Secondly, the interpretation of solvent effects as electrophilic in nature is still controversial in the case of hydroxylic solvents. The ratio c_1/c_2 discussed by Swain, Mosely, and Brown (14) has been assumed to indicate relative sensitivity to solvent nucleophilicity over electrophilicity. However, if this explanation of c_1/c_2 is correct, then it is difficult to explain why the ratio k_{D_2O}/k_{H_2O} for methyl *p*-toluenesulphonate should not lie between those for methyl bromide and *t*-butyl chloride (c_1/c_2 values 2.7, 3.0, and 1.0 respectively).

It is generally accepted that non-electrolytes in water are surrounded by a solvent envelope which melts as the temperature rises, leading to unexpectedly large heat capacity changes (1). Thus for the cumene–water equilibrium at 25°C.,

$$\text{cumene}_{\text{liq.}} \rightleftarrows \text{cumene}_{\text{aq. soln.}}$$

the heat capacity change was found to be +68.8 cal./mol. deg. (2), a value most readily explained in terms of the "melting" of the so-called iceberg

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which forms about the cumene molecule in solution. In the transition state for solvolysis the creation of partial changes will lead to some solvent molecules being more tightly held while the remainder of the envelope will be less ordered than in the initial state.

On the basis of this qualitative picture it is possible to account for several otherwise puzzling phenomena. For example, in the series Me → Et → *i*-Pr benzenesulphonate, the entropies of activation increase (7) (Me, −9.4; Et, −7.5; *i*-Pr, −1.4 e.u.), indicating a trend toward loosening in a series where we would expect the transition to become successively more ionic. This loosening can be attributed to the partial disordering of the residual solvent envelope. At the same time, the heat capacities of activation decrease (11) (Me, −33.4; Et, −37.5; *i*-Pr, −41.4) which can be attributed, on the one hand, to the very tight binding of the ionic solvation and, on the other, to the more nearly water-like state of the residual envelope. Table I shows that the effect of two concurrent processes—tightening and loosening—results in the cancellation of any differences since the ratios k_{D_2O}/k_{H_2O} for the series are the same within experimental error.

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THE OXIDATION OF CARBON MONOXIDE BY SOLID SILVER PERMANGANATE REAGENTS

VI. REACTION KINETICS AND ADSORPTION OF WATER VAPOR[1]

By Morris Katz, R. Riberdy, and G. A. Grant

ABSTRACT

The temperature dependence of the rate constant, k, in the heterogeneous oxidation of carbon monoxide on the surface of silver permanganate – zinc oxide, indicates that in the temperature range of about 11° to 40°C., the process is subject to diffusion or transport control and the experimental activation energy is 1.4 to 1.9 kcal. per mole. In the range of 11° to −3°C. the rate of the surface chemical reaction decreases with a corresponding increase in activation energy to 15 kcal. in this transition stage. At lower temperatures the system is subject to chemical control and E rises to about 27 kcal.

Four adsorption isotherms for water vapor on this reagent have been obtained in the range of −10° to 20°C. The isotherms are sigmoid and indicative of Type II adsorption.

The mechanism of this heterogeneous reaction is discussed on the basis of several possibilities for providing oxygen ions in the electron–ion exchange step of the over-all reaction.

INTRODUCTION

Previous studies by the authors on this gas–solid system have dealt with the kinetics at one influent gas temperature only (10, 11). The kinetics of the reaction in a dynamic system have been found to be similar to the case of irreversible adsorption in a reaction bed such as, for example, the removal of arsine, hydrogen sulphide, and other gases by impregnated charcoal (4). Such systems may be studied successfully by application of the theory of the adsorption wave. A test of this theory has been made by Katz, Grant, and Riberdy (10). The main relations predicted by the theory were found to hold, and the rate constant, k, is independent of the concentration of carbon monoxide in the range where column length and flow rate do not approach critical values. However, the rate constant was found to depend inversely upon the mean granule diameter in contrast to results on charcoal–gas systems where k is apparently independent of granule size.

The extent of adsorption of water vapor by silver permanganate – zinc oxide and its temperature dependence are of interest because preliminary experiments indicated that metallic-oxide-activated silver permanganate preparations are most reactive towards moist gas, and their activity decreases considerably at low relative humidities. The promoting action of water vapor in this case is in marked contrast to the behavior of metallic oxide catalysts of the manganese dioxide – cupric oxide type, i.e. "hopcalites", which are poisoned readily by water vapor and are effective only in dry gas mixtures (15). The promoted argentic oxide of de Boer and van Ormondt (2), on the other hand, is comparable to the silver permanganate – metallic oxide reagents in that it will also oxidize carbon monoxide in moist air.

[1]*Manuscript received September 11, 1956.*
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EXPERIMENTAL METHODS

The reagent used in the following studies contained 69 mole % zinc oxide and 31 mole % silver permanganate in the form of granules of size distribution between −14 to +24 mesh Tyler, prepared by a method outlined in a previous publication (8). Preparation and purification of the carbon monoxide and the apparatus employed to study the reaction kinetics have been described elsewhere (11). The concentration of the escaping carbon monoxide was determined by means of a thermocouple detector cell containing silver permanganate – zinc oxide reagent (12) and calibrated by an iodine pentoxide method (7). The concentrations of gas escaping from the reaction bed could be determined almost instantaneously over the range of 0.001 to 0.1% by this technique.

The reaction cell used in this work was a pyrex glass tube about 15 cm. long and 3.1 cm. inside diameter, with a fritted glass disk of medium porosity sealed into the tube at a point about 3.2 cm. from the bottom. A pair of matched, bead-type thermistors (No. 6014A, Western Electric Co.) were sealed into the side of this tube, the beads being placed in the center of the tube and separated by a distance of 7.5 cm. The hot thermistor was immersed to a depth of 3.0 cm. in the reagent granules. A cold thermistor at the influent end of the tube was immersed in a bed of inactive pumice. Each thermistor, with appropriate variable resistances, formed one arm of a Wheatstone bridge circuit which has been described in a previous paper (13).

The reaction cell was immersed in a constant temperature bath along with a coil of 8 ft. of copper tubing through which the gas–air mixtures were circulated before they entered the reaction cell. The gas concentration, flow rate, temperature of influent gas mixture, and relative humidity of the gas mixture were maintained constant as far as possible in a given experiment.

Experiments were carried out over the temperature range of −10° to 40.0°C. at a flow rate of 4.0 liters per min. at approximately 80% relative humidity. The influence of water vapor at 20°C. on breakdown time, i.e., the time taken for the concentration of the escaping gas to just exceed 10% of the influent concentration, was determined over the range of 15 to 72% relative humidity. Above about 70% relative humidity, there is no appreciable influence of increasing water vapor content of the gas stream on breakdown time.

The water adsorption experiments were carried out by means of a gravimetric method which had the advantage of simulating the dynamic conditions encountered during normal use of the granules in the oxidation of carbon monoxide. Air, at a rate of 4 liters per min., was passed through two long drying towers filled, respectively, with activated alumina and anhydrous magnesium perchlorate. The dry air stream was then passed through a 52 gm. sample of granules (mean diam. 0.91 mm.) for about one and one half hours or until constant weight was attained. The average loss in weight obtained when the sample was dried by this method was 14.1 mgm. compared to 15.6 mgm. when the granules were dried by pumping out for eight hours in a high vacuum at room temperature. There was no measurable difference when nitrogen was substituted for air in the above drying process.

The reaction cell containing the dried sample was immersed in a constant temperature bath, and moist air of known relative humidity passed through the bed at the rate of 4 liters per min. Mixtures of air and water vapor were prepared by metering dry and moist air by means of calibrated flowmeters. Before entering the sample cell, the air mixture was circulated through a series of copper coils immersed in the bath in order to attain the desired temperature. Although less than 15 min. was required for the water adsorption to be substantially completed at each experimental condition, the sample was weighed after each of at least two adsorption periods of 30 min. in order to ensure that the adsorption had reached an equilibrium state.

RESULTS

Dependence of Breakdown Time on Temperature

The breakdown time of a reacting bed of granules has been defined as the time at which the concentration of the escaping gas, c, exceeds an arbitrarily chosen value which in the present experiments was 10% of the influent concentration, c_0. A plot of ln $1/c$ versus the time yields a straight line, if very low escaping concentrations are neglected. The slope of this line represents the value of kc_0 and hence the rate constant k, at each temperature. In experiments at lower temperatures it was found that the escaping concentration of gas was appreciable with an influent concentration of 0.50% for a 3.0 cm. column of reagent, consequently in the runs at −3.0°C. to −10°C. the concentration was reduced to 0.25% in order to keep within the arbitrarily chosen limit for the breakdown time.

The data for a series of experiments are given in Table I. The breakdown time decreases with decreasing temperature at constant influent concentration of gas. Eventually a temperature is reached at which the granules are virtually inactive.

TABLE I

BREAKDOWN TIME, RATE CONSTANT, k, AND ENERGY OF ACTIVATION, E, FOR HETEROGENEOUS OXIDATION OF CARBON MONOXIDE BY SILVER PERMANGANATE – ZINC OXIDE
Experimental conditions: gas stream at 80% R.H. passed through a column, 3.1 cm. in diam., 3 cm. deep, at flow rate of 4 liters per min.

Influent CO concentration, %	Influent gas–air temperature, °C.	Breakdown time (min.) of column (for 90% efficiency)	Rate constant, k, (gm-mol./liter)$^{-1}$ (min.)$^{-1}$	Energy of activation, E, kcal./gm-mol.
0.50	39.8	201	397	1.4
0.50	30.0	187	377	1.4
0.50	21.6	176	351	1.4
0.50	11.3	166	322	1.9
0.50	3.6	152	261	6.4
0.25	−3.0	414	163	15.0
0.25	−6.0	342	108	23.5
0.25	−10.0	140	53	27.3

Temperature Dependence of Rate Constant

A plot of log k against the reciprocal of the absolute temperature yielded the curve shown in Fig. 1. This curve may be divided into three parts. At temperatures above 11°C. the experimental activation energy, E, is only

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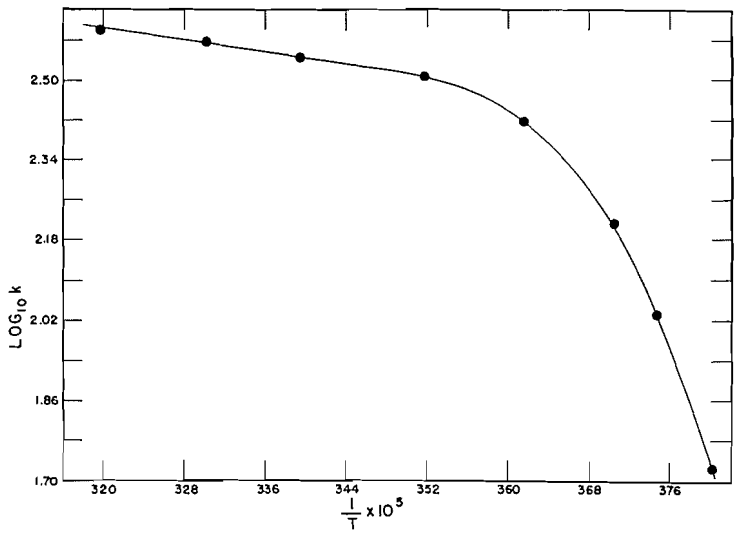

FIG. 1. Temperature dependence of the rate constant in the heterogeneous oxidation of carbon monoxide on silver permanganate – zinc oxide.

about 1.4 kcal. per gm-mol.; a value that is indicative of a purely physical process such as diffusion as the rate controlling step. This confirms the earlier findings on the kinetics of this gas–solid system (10). In the temperature range of about 11° to −3°C. the system passes through a transition state with a corresponding increase in activation energy from 2 to about 15 kcal. per mole. Apparently the rate of the surface chemical reaction, which is extremely fast at high temperatures, decreases appreciably during this transition. As the temperature is decreased beyond this range, the activation energy increases rapidly to over 27 kcal. and the system passes to a process where the observed reaction rate is subject to chemical control.

Influence of Water Vapor on Breakdown Time

Some data on the effect of water vapor in the gas stream on the breakdown time of silver permanganate – zinc oxide in the oxidation of carbon monoxide were presented in an earlier paper (11). With a column length of 5.0 cm. it was shown that the bed life to 90% efficiency of oxidation decreases substantially below 50% relative humidity of the gas–air mixture but very little effect was observed in the range of 50 to 80% relative humidity or higher at 38°C.

Further study of this influence under more critical conditions in a column length of 3.0 cm. and temperature of 20°C., has been made with results as shown in Table II. The present results confirm the earlier findings and indicate clearly that water vapor in optimum amounts increases the speed of the oxidation reaction as well as the life of the reacting bed of granules. The accelerating effect of water vapor has been noted in other heterogeneous oxidation reactions, including the combustion of carbon monoxide by platinum oxide, palladium salts, and gold catalyst.

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TABLE II

EFFECT OF RELATIVE HUMIDITY ON BREAKDOWN TIME, AT 20°C., COLUMN LENGTH 3.0 CM., DIAMETER 3.1 CM.

Air flow rate: 4 liters per min.				Air flow rate: 2 liters per min.			
0.50% CO		0.25% CO		0.25% CO		0.10% CO	
R.H., %	Breakdown time (min.)	R.H., %	Breakdown time (min.)	R.H., %	Breakdown time (min.)	R.H., %	Breakdown time (min.)
72	176	43	410	35	695	20	823
53	163	35	15	20	11	15	70

Adsorption of Water Vapor

The experimental data on the adsorption of water vapor by silver permanganate – zinc oxide granules of average diameter 0.91 mm. are given in Table III. Four adsorption isotherms plotted from these values in the range of −10° to 20°C. are shown in Fig. 2.

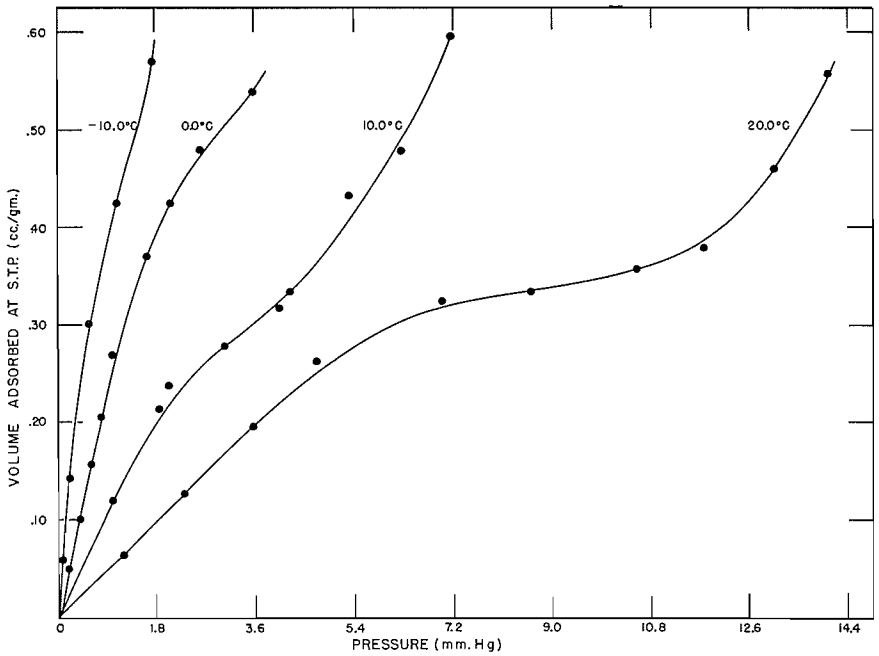

FIG. 2. Experimental adsorption isotherms for water vapor on silver permanganate – zinc oxide.

The results were examined also by the potential theory of Goldmann and Polanyi (5, p. 96). This theory is applicable to both unimolecular and multimolecular adsorption although it does not yield any analytical formulation for the adsorption isotherm. The sole criterion of its validity rests in the accuracy with which it accounts for the temperature dependence of the

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TABLE III

ADSORPTION OF WATER VAPOR ON SILVER PERMANGANATE – ZINC OXIDE

Temperature, °C.	Relative humidity, %	Pressure, mm.	Water vapor adsorbed (S.T.P.) cc./gm.	Water vapor adsorbed gm.×10⁶/gm.
20	7	1.20	.063	50
	13	2.31	.124	100
	21	3.60	.195	157
	27	4.73	.262	211
	40	7.01	.324	261
	49	8.66	.334	269
	60	10.52	.358	288
	67	11.78	.380	306
	74	13.05	.460	370
	80	14.03	.558	449
10	11	1.00	.120	97
	20	1.84	.214	173
	22	2.03	.238	196
	33	3.04	.278	224
	44	4.05	.318	264
	46	4.24	.333	270
	58	5.30	.442	357
	68	6.26	.480	382
	78	7.15	.596	479
0	4	0.20	.050	40
	9	0.40	.100	80
	13	0.60	.155	125
	18	0.80	.205	165
	22	1.00	.270	217
	35	1.60	.370	298
	45	2.08	.425	342
	57	2.60	.480	386
	79	3.60	.540	434
−10	4	0.08	.055	44
	10	0.22	.142	114
	28	0.60	.300	241
	50	1.08	.430	346
	81	1.74	.570	463

adsorption isotherm. The main element of the potential theory is the characteristic curve which permits the calculation of any isotherm at any temperature, if the experimental points, from which this curve is drawn, cover the potential distribution in the entire adsorption space. Usually, such an ideal isotherm is not available in actual practice.

The characteristic curve is shown in Fig. 3. This method is useful in checking the accuracy and reliability of each experimental point of a series of isotherms obtained at different temperatures. Deviations of some of the points from the curve in Fig. 3 may be ascribed to experimental errors.

The isotherms recalculated from the characteristic curve are shown in Fig. 4. It is apparent that the adsorption of water vapor in the lower pressure range is unimolecular with a transition to multilayer adsorption at higher pressures. The isotherms at 20°C. and 10°C. are sigmoid in character but this shape becomes less pronounced at 0°C. and −10°C. All isotherms are

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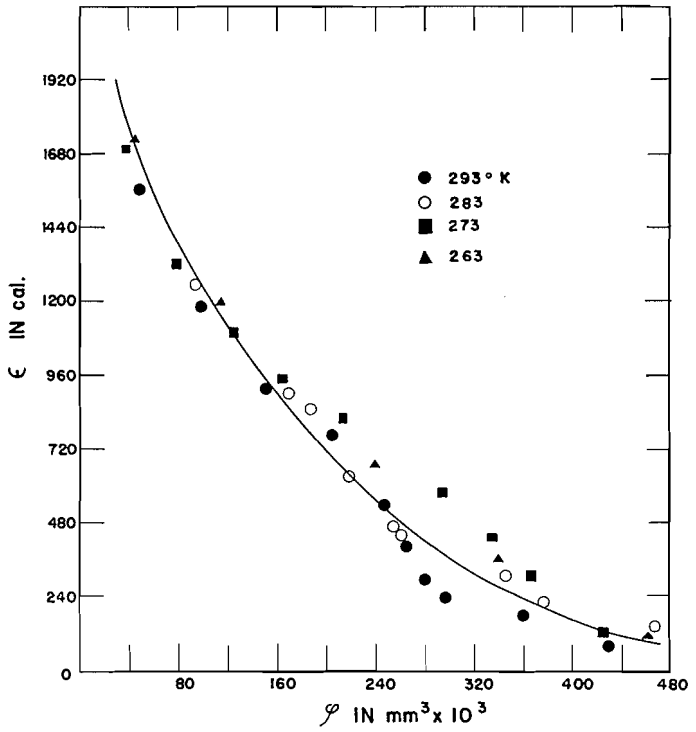

FIG. 3. Characteristic curve for adsorption of water vapor on silver permanganate – zinc oxide.

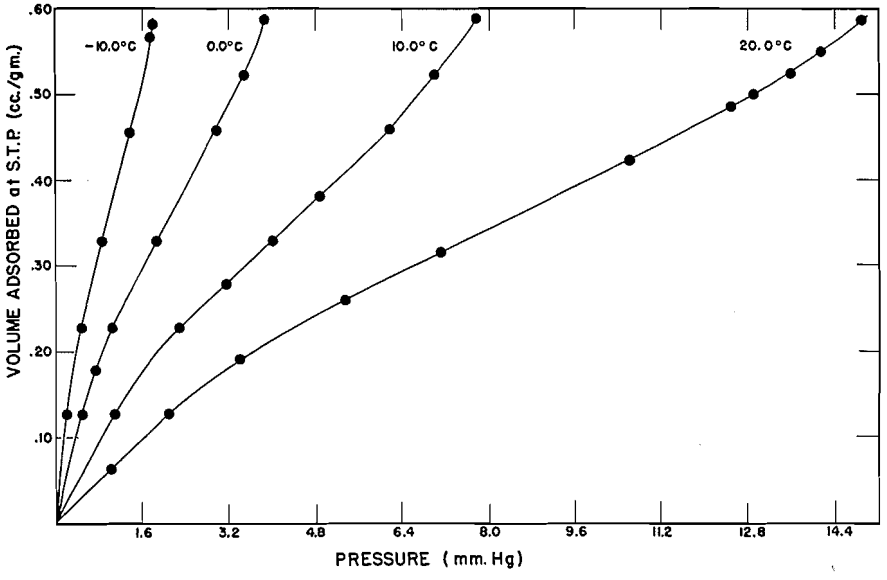

FIG. 4. Adsorption isotherms derived from characteristic curve.

probably indicative of Type II adsorption (Brunauer (3), p. 150) and show that the adsorption of water vapor increases rapidly as the vapor pressure p_0 is approached.

On the assumption of Type II (multimolecular) adsorption, the volume of water vapor adsorbed by the silver permanganate – zinc oxide, when the surface is covered by a monolayer, has been calculated from the adsorption isotherms of Fig. 4 to be, on the average, 0.218 cc./gm. This yields a value of about 0.7 sq. meter/gm. for the surface area of granules 0.91 mm. in diameter. The original, experimentally derived, isotherms yielded a value of about 1.0 sq. meter/gm. Independent measurements of surface area by the B.E.T. nitrogen adsorption method was reported earlier as 1.4 sq. meter/gm. (10) for this reagent, for granules of similar size.

DISCUSSION

An explanation for the form of the curve depicting the temperature dependence of the rate constant may be obtained from a consideration of the temperature coefficient of heterogeneous reactions. This subject has been reviewed recently by Riddiford (18) and by Bircumshaw and Riddiford (1). For certain systems the observed reaction rate is determined solely by the rate of the transport or diffusion process to surface of the solid, whereas for other systems the observed rate is subject to "activation" or chemical control. There is also the possibility of systems of intermediate type for which the observed rate is a function of both the rate of the chemical reaction at the surface and of the rate of the transport process.

Riddiford has shown that for the intermediate type of reaction in the steady state, the observed velocity constant, k, is related to the rate constant of the surface chemical reaction, k_c, and the rate constant of the transport process, k_t, by the following expressions:

$$k = k_t k_c/(k_t+k_c). \qquad [1]$$

If k_t is very much greater than k_c, the observed rate will be determined solely by the rate of the surface chemical reaction; on the other hand, if k_t is very much less than k_c, the case will be that of transport control.

The following equation expresses the dependence of the observed rate constant on temperature, assuming that both k_c and k_t vary exponentially with temperature, T:

$$\frac{d(\ln k)}{dT} = \frac{1}{RT^2}\left[\left(\frac{k_c}{k_t+k_c}\right)E_t+\left(\frac{k_t}{k_t+k_c}\right)E_c\right]. \qquad [2]$$

If an experimental energy of activation, E, is defined by the relation $d(\ln k)/dT = E/RT^2$, then E may be determined at any value of T from the slope of the curve. From Equation [2]

$$E = \left(\frac{k_c/k_t}{1+k_c/k_t}\right)E_t+\left(\frac{1}{1+k_c/k_t}\right)E_c, \qquad [3]$$

and the variation of E with temperature is governed by the variation of the ratio k_c/k_t.

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In actual practice, E_c and E_t will have different values (neglecting the special case where $E = E_c = E_t$). Two cases may therefore be considered: (1) $E_c < E_t$, which corresponds to the condition $k_c \gg k_t$ at all temperatures, and hence $E = E_t$ at all temperatures; (2) $E_c > E_t$, which indicates that the observed rate will be subject to chemical control at low temperatures and transport control at higher temperatures. For case 2, a sufficient change in temperature will result in a shift of control.

The change in slope of the plot of ln k on $1/T$, in Fig. 1, is therefore an example of case 2, above, the rate of oxidation of carbon monoxide being controlled by the mass transfer of gaseous reactants to the surface in the temperature region above about 10°C., a purely physical process with a low energy of activation. Below 10°C. there is a pronounced shift in control towards the surface chemical reaction. A somewhat similar transition in control has been noted by Tu, Davis, and Hottel (20) in studies on the rate of combustion of carbon spheres in a flowing air stream. Another case is that of the catalytic oxidation of sulphur dioxide on platinum pellets (17).

Pure silver permanganate in the dry state is virtually unreactive toward carbon monoxide and only a comparatively slow reaction, preceded by an induction period, is evident when the crystals contain from about 5 to 10% moisture. When the salt is deposited on a weakly basic or weakly acidic metallic oxide carrier in the correct proportions, the resulting preparations become highly activated. An extremely fast oxidation reaction then takes place in the presence of the dry reagents at room temperature or lower, provided some water is present in the vapor phase (9, p. 191; 11). Water evidently acts as a promoter after being adsorbed on the surface of the solid silver permanganate reagent. The results on the temperature dependence of the water adsorption isotherms indicate that the adsorption is of the van der Waals type and the amount adsorbed is relatively small in the partial pressure range corresponding to 0–80% relative humidity of the gas stream. This is to be expected from the non-hygroscopic nature of the granules and the comparatively low surface area.

It is suggested that the role of adsorbed water, in the oxidation of carbon monoxide by silver permanganate – zinc oxide, is to assist in the formation of oxygen ions. Probably, a hydrate ($ZnO.H_2O$) is formed first at points on the crystal surface with subsequent formation of (OH) groups, because of the weakly basic property of the oxide.

There are three possibilities by which oxygen ions may be provided for the oxidation of carbon monoxide in the electron–ion exchange step of the over-all reaction:

(*a*) The ions may be derived from the silver permanganate lattice sites, resulting in a surface chemical reaction in which the silver salt is reduced. Since the reduced salt cannot be regenerated, this step would not lead to catalysis.

(*b*) In a catalytic reaction, the oxidation of carbon monoxide could take place with oxygen ions derived from the defective zinc oxide crystal lattice, especially at the interface between the oxide and the silver salt.

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The regeneration of the catalyst would require that the vacant lattice sites be replenished by clearage of adsorbed oxygen molecules to form ions and migration of such oxygen ions into the lattice vacancies.

Substantially similar mechanisms for the catalytic oxidation step in the presence of a semi-conductor, such as zinc oxide, have been propounded by Weyl (21, p. 87) and by Schwab and Block (19).

$$CO + (cat.) \rightarrow CO^+ + (cat. + (e))$$
$$CO^+ + O^- \rightarrow CO_2$$
$$O_2(ads.) + 2(e)^- \rightarrow O^- + O^-$$
$$2\,O^- (ads.) \rightarrow O_2\,(gas) + 2(e)$$

(*c*) A hydrate, such as $ZnO.H_2O$, may form initially with subsequent formation of (OH) groups and oxygen ions. In the case of a platinum dioxide catalyst, the formation of a hydrate, $PtO_2.H_2O$, by adsorption of water, has been found to accelerate considerably the reduction of the oxide by carbon monoxide so that the reaction takes place at room temperature or lower (16). This is true also for the present silver permanganate reagent.

It has been shown by Katz *et al.* in an earlier paper (14) that the oxidation of carbon monoxide in air by silver permanganate – zinc oxide takes place according to both a stoichiometric reaction, involving the reduction of approximately one molecule of the silver permanganate per molecule of CO, and a catalytic reaction with oxygen from the gas phase. From a mass balance of the reactants and chemical analysis of the products, it was found in experimental runs that the reaction path was about evenly divided between the stoichiometric and catalytic processes, provided the efficiency of oxidation in the reacting column did not fall below 90% of its initial value. Below 90% efficiency, a greater proportion of the CO was oxidized stoichiometrically.

Recent studies by Grant and Katz (6) on the thermal decomposition of pure silver permanganate at 100°C. indicate from analysis of the reaction products that 2 moles of silver permanganate yield 1.2 moles of oxygen in a mechanism involving three steps. Such a mechanism could supply from 51 to 78% of the oxygen required in the oxidation of CO, whereas in oxidation experiments, under conditions indicated above, the actual weight of oxygen lost by the $AgMnO_4$ varied from 46.6 to 55.0% of that required for reaction with the carbon monoxide, the remainder being supplied from the gas phase.

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L'OXYDATION STOÏCHIOMÉTRIQUE DE L'OXYDE D'AZOTE PAR L'OZONE ÉTABLIE PAR PHOTOMÉTRIE DU BIOXYDE D'AZOTE[1]

PAR GUY G. GOYER

RÉSUMÉ

La réaction a été étudiée par photométrie. La concentration du bioxyde d'azote, et conséquemment le rendement de l'oxydation de l'oxyde d'azote, a été déterminée par transmission lumineuse. La concentration des ingrédients du mélange gazeux a été variée entre de vastes limites: l'oxyde d'azote de 0.05% à 13.3% v/v, l'oxygène de 1.5% à 33% et l'azote de 63% à 98.4% sous une humidité relative variant de 0 à 62%.

L'ozone à des concentrations variant de 0 à 1.3% v/v était introduit dans ces mélanges gazeux et la quantité de bioxyde d'azote produit par ce traitement était mesurée quantitativement. On appliqua une correction pour toute formation parallèle de bioxyde d'azote résultant de la réaction normale et lente entre l'oxyde d'azote et l'oxygène. La quantité de bioxyde d'azote formé par molécule d'ozone ajoutée était une mesure directe de la longueur de la chaîne d'oxydation. Des 54 mesures acceptées, 34 ont été faites sur des gas secs et 20 ont été faites sur des gas humides. Les rapports [bioxyde d'azote]/[ozone] obtenus varient entre 0.7 et 1.15, donnant une moyenne de 0.95 ± 0.1. L'addition de vapeur d'eau au mélange gazeux n'a pas appréciablement changé les résultats obtenus. Un rapport $[NO_2]/[O_3]$ plus grand que 1.15 n'a jamais été obtenu sous les conditions étudiées.

INTRODUCTION

L'oxydation de l'oxyde d'azote par l'oxygène est connue comme étant un procédé plutôt lent. Cependant, Zabolotskii rapporta en 1950, que l'ozone pur initie des chaînes de réaction entre l'oxyde d'azote et l'oxygène. Il soutint que la quantité d'ozone utilisée pour l'oxydation de l'oxyde d'azote est considérablement moindre que la quantité requise par la réaction stoïquiométrique suivante

$$NO + O_3 \rightarrow NO_2 + O_2$$

où le rapport [bioxyde d'azote]/[ozone] est égal à l'unité. Par exemple, Zabolotskii rapporta que l'oxydation, à température ambiante et sous pression atmosphérique, d'un mélange d'air et d'oxyde d'azote contenant 13.2% d'oxyde d'azote, 18.3% d'oxygène et 68.5% d'azote atteignit un rendement de 80% tandis que sous les mêmes conditions, l'oxydation d'oxyde d'azote avec de l'air ozonisé atteignait 100%. Dans ce cas, un rapport de 72 est atteint, c'est-à-dire qu'une molécule d'ozone est responsable de l'oxydation de 72 molécules d'oxyde d'azote. Cependant, l'effet catalytique de l'ozone n'avait été confirmé par aucune autre investigation au début de 1955 comme une récente recherche de la littérature l'a démontré. Conséquemment, une vérification expérimentale de l'hypothèse de Zabolotskii semblait indiquée. L'objet du présent travail était donc d'étudier l'effet de l'ozone sur la réaction entre l'oxyde d'azote et l'oxygène dans un vaste intervalle de concentration d'oxyde d'azote à température ambiante et sous pression atmosphérique.

[1]*Manuscrit reçu le 3 juillet 1956.*
Contribution de Canadian Industries Limited, Central Research Laboratory, McMasterville, Qué.

MÉTHODE EXPÉRIMENTALE

1. *Description de l'Appareil*

(*a*) *Photomètre*

Un photomètre I (figure 1) a été construit dans nos laboratoires pour étudier la concentration du bioxyde d'azote. Le système optique consiste essentiellement en un faisceau lumineux émis par une lampe d'automobile (G.E.–1130), filtré par un filtre violet de 4 mm. d'épaisseur (Corning 5113) et dirigé sur une cellule photoélectrique RCA–929. Le courant produit par la cellule photoélectrique et amplifié par un amplificateur électronique *L* sert

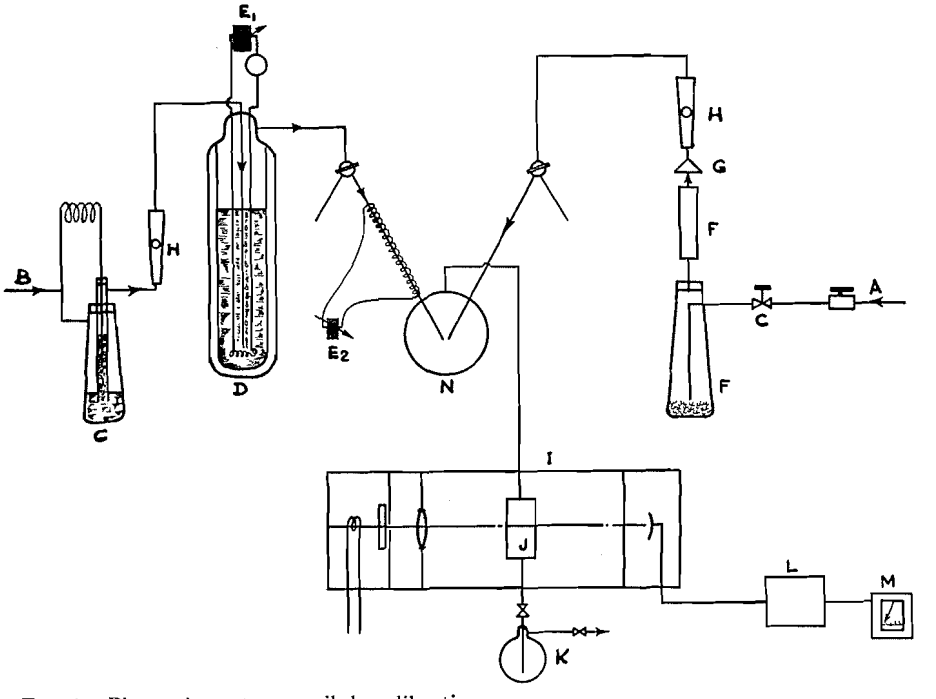

FIG. 1. Photomètre et appareil de calibration.
A—air; *B*—azote; *C*—régulateur de pression; *D*—NO_2 liquide; *E*—éléments chauffants; *F*—déssechants; P_2O_5 et $CaCl_2$; *G*—filtre; *H*—compteurs de débit; *I*—photomètre; *J*—cellule; *K*—ballon d'échantillonnage; *L*—amplificateur; *M*—enrégistreur; *N*—mélange des gaz, air et NO_2.

à actuer un milliampèremètre enrégistreur *M* (Esterline-Angus, 0 à 1.0 milliampère d-c. modèle AW). La stabilité de l'instrument est assurée par un régulateur de voltage Sola dans le circuit de l'amplificateur et de la source lumineuse.

Le vaste intervalle de concentration de bioxyde d'azote impliqué dans ce travail a nécessité l'emploie de deux cellules de transmission *J*. Une courte cellule de verre, 2.8 cm. de diamètre par 2 cm. de long, a servi à déterminer les concentrations entre 0.2% et 13% v/v. L'intervalle inférieur, de 0 à 0.5% a été étudié dans une longue cellule, 3.8 cm. de diamètre par 100 cm. de long. La courte cellule a été modifiée au cours de ce travail pour permettre le mé-

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lange des gaz à l'intérieur même de la cellule. Cette modification a été rendue nécessaire par la vitesse, très considérable aux hautes concentrations d'oxyde d'azote, de l'oxydation de l'oxyde d'azote par l'oxygène. Le système optique, ainsi que les deux cellules, était inséré dans un cabinet à l'épreuve de la lumière.

Le photomètre a été calibré par analyse chimique. La concentration totale d'oxyde d'azote dans un échantillon de mélanges gazeux soumis au photomètre à été déterminée chimiquement et rapportée sur un graphique en fonction de la transmission lumineuse. Tel qu'indiqué sur la figure 1, les mélanges gazeux ont été préparés par vaporisation de bioxyde d'azote liquide *D*, dans un courant lent d'azote sec et par la dilution du riche mélange ainsi obtenu dans un large volume d'air sec et filtré *N*. Sous un débit constant d'azote et d'air, le mélange était enrichi en bioxyde d'azote par l'élévation de la température du bioxyde d'azote liquide à l'aide d'un élément chauffant E_1. La condensation du bioxyde d'azote sur les parois de la canalisation du mélange riche a été prévenue à l'aide d'un élément chauffant E_2, sur la canalisation elle-même. La température des gaz était mesurée, après mélange, à l'aide d'un thermomètre. Le mélange gazeux s'écoulait à travers la cellule de transmission lumineuse *J* vers un ballon calibré pour l'échantillonnage *K*. Après quelques minutes d'opération, l'équilibre thermique était atteint dans le système entier et le photomètre indiquait alors une transmission constante. Un échantillon de gaz était alors obtenu et absorbé dans un mélange d'acide sulfurique et de permanganate de potassium et analysé pour déterminer les oxydes d'azote (11). Des ballons d'échantillonnage de 200 cc. fûrent employés pour les mélanges riches, analysés dans la courte cellule, et de 5 litres pour les mélanges plus dilués, analysés dans la longue cellule. L'absorption complète des oxydes d'azote dans le mélange gazeux était assurée par une agitation énergique des ballons pendant environ 12 heures.

L'appareil utilisé pour les mesures d'oxydation était en tout point semblable à celui employé dans la calibration. Dans le premier cas, le bioxyde d'azote liquide est remplacé par l'oxyde d'azote gazeux et l'air par l'azote. Le mélange d'oxyde d'azote à l'azote était effectué dans un ballon mais l'oxygène n'était ajouté à ce mélange primaire qu'à l'entrée de la longue cellule ou directement à l'intérieur de la courte cellule. Pour un mélange rapide et complet, la rencontre des deux courants gazeux s'effectuait à angle droit. Les trois courants gazeux étaient controllés par des régulateurs de pression *C*, et mesurés par des compteurs calibrés de débit gazeux *H*.

(*b*) *Ozonateur*

Un ozonateur Welsbach (Model T–23) (6) a été utilisé avec un courant d'oxygène comme source d'ozone. L'appareil était refroidi par de l'eau courante. La canalisation de l'ozone était en acier inoxydable.

L'ozone a été analysé par la méthode conventionnelle à l'iodure de potassium (12). De 1 à 3 litres d'oxygène ozonisé étaient absorbés lentement dans approximativement 150 cc. de solution à 2% d'iodure de potassium. La solution résultante était alors acidifiée et titrée pour l'iode avec du thiosulfate

de sodium, 0.1 normal, à l'aide d'amidon comme indicateur. L'accord entre les déterminations successives était d'environ 1%.

2. Procédé

(*a*) *Calibration du photomètre*

Les résultats de l'analyse chimique des échantillons gazeux étaient tout d'abord exprimés en moles de bioxyde d'azote dans le volume connu d'échantillon et par la suite réduit en moles par litre. Cependant, une partie du bioxyde d'azote révélé par analyse chimique apparaissait dans la cellule de transmission à l'état de tétroxyde d'azote transparent, à cause de l'équilibre instantané bien connu entre ces deux oxydes d'azote (1, 4, 13, 14). Conséquemment, l'effet de cette réaction secondaire a été incorporé dans la calibration par le calcul des concentrations d'équilibre du bioxyde d'azote (NO_2 "optique") et de tétroxyde d'azote en fonction du volume pourcent de bioxyde "chimique" ($NO_2 + 2N_2O_4$), figure 2. Les transmissions observées et calculées furent alors rapportées sur les graphiques de calibration en fonction du bioxyde chimique.

Les concentrations d'équilibre de bioxyde et de tétroxyde d'azote dans les mélanges gazeux employés ont été calculées entre des limites de concentrations de bioxyde chimique variant de 0.005% à 13% par volume à 20°C. et à 25°C. à pression atmosphérique. Cette réaction est bien connue. Les constantes d'équilibre en fonction de la température ont été mesurées par plusieurs chimistes et leurs résultats sont en accord satisfaisant (1, 4, 13, 14). Les concentrations d'équilibre peuvent être calculées pour tout mélange gazeux, avec ou sans gaz inerte, par une méthode d'approximation successive selon le procédé suivant.

Dans un mélange de x mole de bioxyde et $(100-x)$ mole de gaz inerte la polymérisation réduit le bioxyde à $(x-z)$ mole et forme $z/2$ mole de tétroxyde. A l'équilibre, le nombre total de moles dans le mélange gazeux est donné par

$$\begin{array}{cccc} \text{Inerte} & NO_2 & N_2O_4 & \text{Total} \\ (100-x) & +(x-z) & +z/2 & =100-z/2. \end{array}$$

Si la pression totale est d'une atmosphère, les pressions partielles sont

$$NO_2 = (x-z)/(100-z/2) \text{ ats.}$$

$$N_2O_4 = z/[2(100-z/2)] \text{ ats.}$$

et les constantes d'équilibre sont données par

$$K_p = \frac{p_{N_2O_4}}{p^2_{NO_2}} = \frac{z}{2(100-z/2)} \cdot \frac{(100-z/2)^2}{(x-z)^2}$$

i.e.,

$$K_p = \frac{z(100-z/2)}{2(x-z)^2}$$

ou x est la concentration en volume des oxydes d'azote à l'état de bioxyde, c'est-à-dire la concentration en volume du bioxyde chimique. Cette équation

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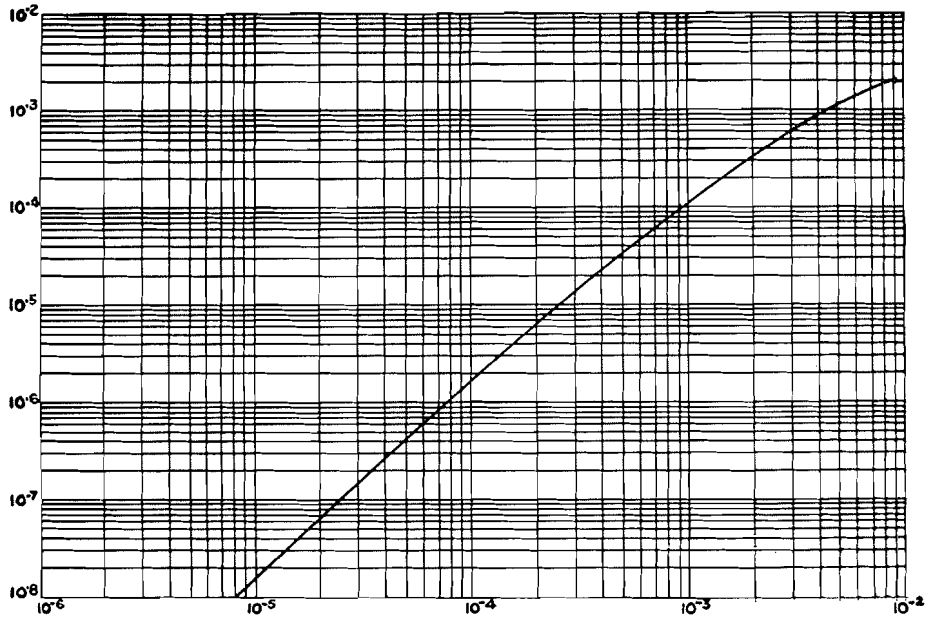

FIG. 2. L'équilibre $2NO_2 \rightleftharpoons N_2O_4$ à la pression atmosphérique et à 25°C.
Ordonnée: $[N_2O_4]$ moles/litre.
Abscisse: NO_2 "chimique" $[NO_2 + 2N_2O_4]$ moles/litre.

peut être résolue en fonction de z par approximation successive. Les résultats à 25°C. sont présentés sur la figure 2.

Une courbe de transmission théorique, intégrée dans l'intervalle de longueurs d'onde transmises par le filtre et basée sur les caractéristiques de la cellule photoélectrique, a été calculée en fonction de la concentration du bioxyde d'azote à l'aide de l'équation de Beer.

$$1/T = I_0/I = 10^{kcd}$$

ou T est la transmission,

I_0, I sont les intensités incidentes et transmises, respectivement,

k est le coefficient d'absorption pour NO_2,

c est la concentration de NO_2 optique en mole/litre,

et d est la longueur de la cellule en cm.

La méthode d'intégration graphique employée dans le calcul des transmissions théoriques est la suivante: tout d'abord la réponse de la cellule photoélectrique RCA–929 employée dans le photomètre, à l'énergie émise par une source au tungstène à 2870° K., a été rapportée en fonction de la longueur d'onde d'après les données du manufacturier.

La transmission du filtre employé (4 mm. Corning 5113) (2) s'étend entre 350 mμ et 480 mμ. Le produit de la réponse de la cellule photoélectrique par la transmission du filtre à une longueur d'onde donnée donne la réponse du photomètre entier à travers des cellules vides. Les courbes "zèro" NO_2 (figures 6 et 7) ont été obtenues de cette façon pour tout l'intervalle de longueurs d'onde transmises par le filtre.

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Les coefficients d'absorption du bioxyde d'azote dans l'intervalle de longueurs d'onde considérées ont été obtenus des données de Hall et Blacet (5). Après avoir traduit leurs résultats en des unités comparables, les coefficients d'absorption publiés par Hall et Blacet (5), par Holmes et Daniels (7) et par Dixon (3) ont été trouvés en accord quasi-parfait. Les coefficients d'absorption à six longueurs d'onde ont été obtenus d'une courbe unie tracée sur la courbe à structure fine publiée par Hall et Blacet. La longueur d'onde, le coefficient d'absorption de NO_2 et la réponse du photomètre aux longueurs d'onde choisies sont donnés dans le Tableau I.

TABLEAU I

DONNÉES EMPLOYÉES DANS LES CALCULS DE TRANSMISSIONS

Longueur d'onde	Coéfficient d'absorption, mole^{-1} litre cm.$^{-1}$	Réponse, unités arbitraires
366	130	1.34
405	145	14.66
415	148	16.40
425	146	16.34
436	138	14.18
460	121	5.5

Les transmissions ont été calculées à six longueurs d'onde pour plusieurs concentrations de bioxyde d'azote. Dans le cas de la cellule de 2 centimètres, des concentrations de 5, 10, 15, 20, 30 et 40×10^{-4} moles/litre ont été étudiées et sont présentées sur la figure 7. Pour le cas de la longue cellule, les transmissions ont été calculées pour des concentrations de 10, 20, 30 et 40×10^{-6} moles/litre comme le démontre la figure 6. Le produit de la transmission obtenue par la réponse du photomètre à travers des cellule vides donne la réponse du photomètre à travers différentes concentrations de bioxyde pour l'intervalle de longueurs d'onde transmises.

Les surfaces limitées par chacune des courbes ont été mesurées à l'aide d'un planimètre Ott. La transmission totale d'une concentration donnée, soit 20×10^{-4} moles/litre, est le rapport de la surface limitée par la courbe de 20×10^{-4} moles/litre à la surface limitée par la courbe à 0 moles/litre. Les transmissions intégrées ainsi obtenues ont été rapportées pour des concentrations de 5, 10, 15 et 20×10^{-4} moles/litre (6.1, 13.3, 22.4 et 33.5×10^{-4} moles/litre NO_2 chimique) sur la figure 3. Sur la figure 4, les transmissions théoriques sont rapportées pour des concentrations de 10, 20, 30 et 40×10^{-6} moles/litre (10, 20.1, 30.3 et 40.6×10^{-6} moles/litre NO_2 chimique).

Malgré les incertitudes provenant de l'emploi des données du manufacturier pour la réponse de la cellule photoélectrique et pour la transmission du filtre, l'accord entre les transmissions calculées et les transmissions obtenues expérimentalement est remarquable, spécialement dans le cas de la cellule de 100 centimètres où la concentration d'équilibre du tétroxyde est presque négligeable.

La figure 3 illustre la calibration finale de la cellule de 2 centimètres et la

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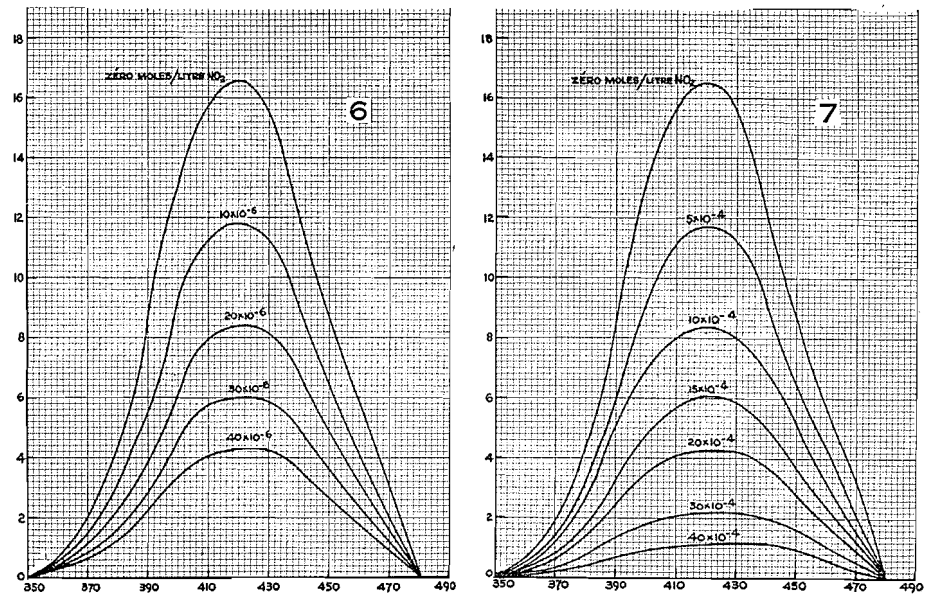

FIG. 6. Réponse du photomètre en fonction de la concentration du NO_2 et de la longueur d'ondes de la lumière incidente. Cellule de 100 cm.
Ordonnée: Unités arbitraires.
Abscisse: Longueur d'ondes mμ.

FIG. 7. Réponse du photomètre en fonction de la concentration du NO_2 et de la longueur d'ondes de la lumière incidente. Cellule de 2 cm.
Ordonnée: Unités arbitraires.
Abscisse: Longueur d'ondes mμ.

figure 4 celle de la cellule de 100 centimètres. Dans les limites de concentrations indiquées, la loi de Beer est confirmée en accord avec les récentes données de Norris (10) et de Hall (5). Aux plus hautes concentrations cependant (figure 3) la droite prédite par la loi de Beer entre la concentration et la transmission est masquée par l'équilibre

$$2NO_2 \rightleftharpoons N_2O_4.$$

Cependant, une relation linéaire est obtenue si la transmission est rapportée en fonction de la concentration du bioxyde optique, comme dans la figure 5, plutôt qu'en fonction de la concentration du bioxyde chimique.

L'accord obtenu entre toutes les méthodes de calcul ou de mesure de la concentration du bioxyde d'azote est démontré sur une courbe de calibration (figure 4). La déviation moyenne de $\pm 10\%$ pour les 16 mélanges utilisés pour la calibration est légèrement supérieure à la déviation de $\pm 8\%$ publiée par Norris (10). Les fluctuations légères de température entre le mélange et l'échantillonnage peuvent expliquer cette différence.

(*b*) *Mesures d'ozonisation*

Toutes les mesures d'ozonisation ont été effectuées sur des systèmes dynamiques. Après avoir permis au circuit photométrique d'atteindre son équilibre thermique, la circulation d'azote sec et d'oxygène était établie à travers la cellule de transmission. Après l'obtention d'une transmission constante

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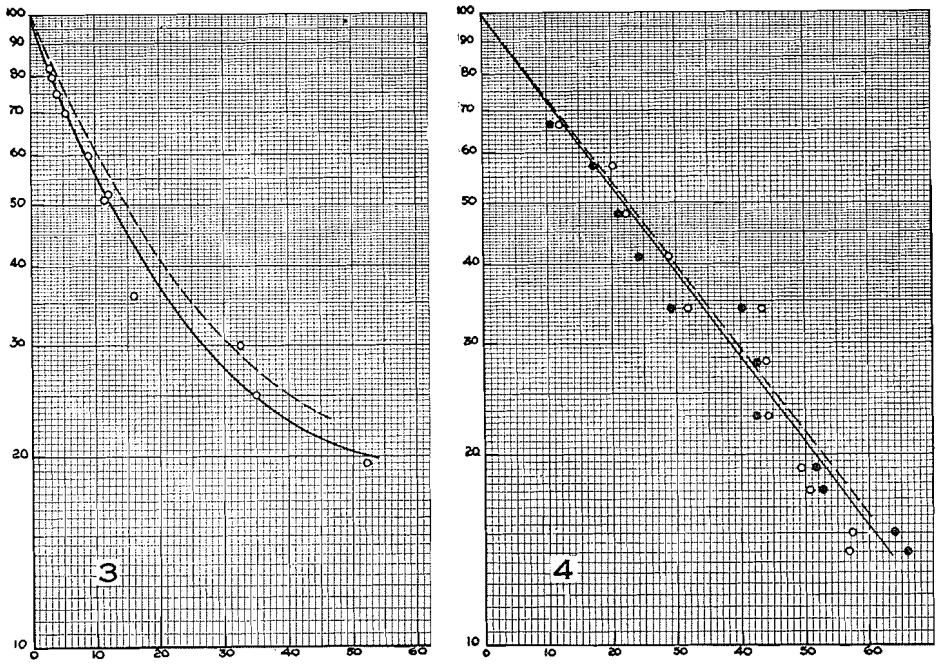

FIG. 3. Courbe de calibration du photomètre. Cellule de 2 cm.
———Concentrations obtenues par analyse chimique.
– – –Concentrations calculées d'après les propriétés optiques du systême.
Ordonnée: Transmission %.
Abscisse: NO_2 "chimique" $[NO_2 + 2N_2O_4]$ moles/litre $\times 10^4$.

FIG. 4. Courbe de calibration du photomètre. Cellule de 100 cm.
○Concentrations obtenues par analyse chimique.
●Concentrations calculées d'après les débits relatifs des gaz.
– – –Concentrations calculées d'après les propriétés optiques du système.
Ordonnée: Transmission %.
Abscisse: NO_2 "chimique" $[NO_2 + 2N_2O_4]$ moles/litre $\times 10^6$.

l'enregistreur était ajusté à 0% et à 100% de transmission. L'oxyde d'azote était alors ajouté au courant d'azote dans des proportions connues pour obtenir un mélange propice à l'étude. Le photomètre répondait alors en indiquant une transmission inférieure caractéristique non seulement de la concentration absolue du monoxyde et de l'oxygène mais aussi caractéristique du débit du mélange gazeux à travers la cellule. L'ozone était ajouté au mélange après la détermination de la concentration du bioxyde, produit par l'oxydation du monoxyde par l'oxygène durant le temps de réaction, depuis le mélange des gaz jusqu'à la mesure de leur transmission. L'effet d'une quantité connue d'ozone sur l'oxydation d'une quantité connue de monoxyde d'azote était alors déterminé par la différence entre les deux mesures consécutives de transmission. Habituellement chaque mélange gazeux était soumis à l'action de quatre différentes concentrations d'ozone. La composition du mélange original était de plus toujours déterminée à la fin de chaque expérience en permettant au mélange dans la cellule de s'oxyder complètement. L'accord était satisfaisant. A cause de l'augmentation de la vitesse d'oxydation du monoxyde par l'oxygène avec l'augmentation de la concentration du monoxyde (1), le

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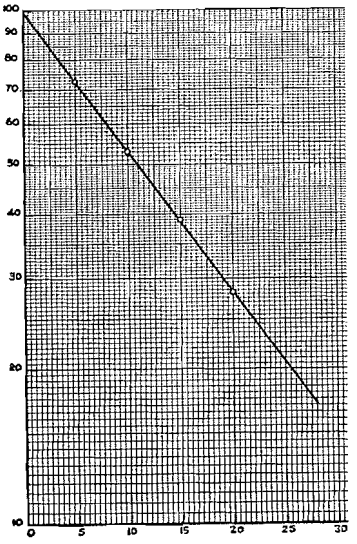

FIG. 5. Transmission de la lumière (350 à 480 mμ) par le NO_2.
Ordonnée: % Transmission.
Abscisse: NO_2 "optique" mole/litre $\times 10^4$.

débit du mélange gazeux a été augmenté de 2 à 4 litres par minute pour les mélanges dilués et de 4 à 7 litres par minute pour les plus riches, de façon à obtenir une transmission initiale considérable. Conséquemment, le temps de réaction alloué aux mélanges riches avant la mesure de la transmission était d'environ 0.10 seconde comparé à environ 25 secondes pour les mélanges dilués.

Cependant, cet effet était presqu'entièrement contrebalancé par la grande concentration d'oxygène nécessaire à la production suffisante d'ozone pour produire un effet sur la courbe de transmission. De plus, le débit maximum de mélange gazeux était limité par le débit maximum d'ozone. Conséquemment, pour les mélanges riches, le temps de réaction était court, la vitesse de réaction était grande, à cause de la haute concentration de monoxyde d'azote et d'oxygène, et l'effet de l'ozone était petit à cause de la petite quantité relative d'ozone qui pouvait être ajoutée aux mélanges gazeux avec l'instrument employé. D'où la difficulté de mesurer avec précision la petite différence entre les transmissions produites par les mélanges oxygénés et celles produites par les mélanges ozonizés. Cette piêtre précision explique les rapports $[NO_2]/[O_3]$ théoriquement impossibles obtenus, pour la plupart, à de hautes concentrations de monoxyde d'azote. Pour les basses concentrations, il était toujours possible d'augmenter ce rapport à l'unité, mais jamais beaucoup plus haut, en augmentant le débit du mélange gazeux.

Des gaz humides ont aussi été employés dans quelques expériences. Dans ce cas, l'azote était humidifié dans un laveur à gaz et filtré par un filtre "millipore". L'humidité relative était calculée par des mesures de température de condensation.

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RÉSULTATS EXPÉRIMENTAUX

Quatre-vingt-dix mesures ont été obtenues, dont 36 ont été rejetées à cause de conditions expérimentales inadéquates. Sur les 54 mesures acceptées, 34 ont été faites sur des gaz secs et 20 sur des gaz humides. Comme le démontre le Tableau II, les concentrations relatives des gaz ont été variées entre de vastes limites dans les mélanges employés.

TABLEAU II

MESURES D'OZONISATION SUR DES GAS SECS; TEMPÉRATURE AMBIANTE, PRESSION ATMOSPHÉRIQUE

Concentration des gaz, % v/v				Nombre de mesures	$\frac{[NO_2]}{[O_3]}$
NO	O_3	O_2	N_2		
0.05	0.002–0.018	1.56–12.5	98.4–87.4	4	1.12
0.10	0.003–0.091	2.5–5	97.5–95.0	5	0.98
0.12	0.014–0.115	1.6–12.5	98.3–87.3	4	1.01
0.17	0.02–0.082	2.95–12.5	97–87.4	3	0.97
2.03	0.16–1.28	4.1–33.3	93.6–63.3	4	0.81
3.9	0.06–0.17	4.22	91.7	3	0.94
4.8	0.05–0.17	4.22	90.8	3	1.15
6.1	0.29–0.53	15.9	77.5	2	0.93
13.3	0.06–0.64	18.2	68.0	6	0.49

Dans tous les cas, la concentration d'ozone variait depuis des traces jusqu'à des quantités appréciables. Une chaîne de réaction n'a jamais été observée sous aucune condition étudiée. Les difficultés expérimentales rencontrées dans l'étude des mélanges riches, tel que discutées précédemment, sont démontrées par les rapports observés pour des concentrations de monoxyde de 13.3% et 10%. Dans ces cas il a été impossible, avec l'instrument employé, d'augmenter la sensibilité des mesures au point d'obtenir un rapport approchant l'unité. Cependant, il est logique de présumer une telle possibilité sous des conditions propices de débit comme fut le cas pour tous les mélanges dilués.

Le Tableau III donne des résultats similaires pour les gaz humides.

TABLEAU III

MESURES D'OZONISATION SUR DES GAZ HUMIDES; TEMPÉRATURE AMBIANTE, PRESSION ATMOSPHÉRIQUE

Humidité, %	Concentration des gaz, % v/v				Nombre de mesures	$\frac{[NO_2]}{[O_3]}$
	NO	O_3	O_2	N_2		
38	13.3	0.06–0.64	18.2	68	4	0.48
53	10	0.06–0.64	16	74	4	0.70
44	5	0.03–0.35	10	85	4	1.04
62	1	0.007–0.7	2	97	4	0.79
59	0.5	0.007–0.7	2	97.5	4	0.99

La comparaison des deux tableaux ne démontre aucune différence appréciable entre les résultats pour des gaz secs ou humides. A l'exception de ceux obtenus aux très hautes concentrations de monoxyde d'azote les rapports [bioxyde d'azote]/[ozone] s'étendent entre 0.7 et 1.15 et donnent une moyenne de 0.95 ± 0.1.

Une réaction en chaîne n'a jamais été obtenue au cours de ce travail. Des rapports inférieurs à l'unité ont été obtenus en maintes occasions à cause de limitations instrumentales et ont pu être corrigés dans presque tous les cas. Cependant aucune détermination n'a conduit à un rapport supérieur à 1.15.

DISCUSSION DES RÉSULTATS

En 1950 Zabolotskii publiait une courte communication (15) sur le rôle catalytique de l'ozone dans l'oxydation de l'oxyde d'azote par l'oxygène. Il soutenait alors que la quantité d'ozone employée dans l'oxydation de l'oxyde d'azote est considérablement inférieure à la quantité requise par la réaction stoïchiométrique,

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad [1]$$

où le rapport [bioxyde d'azote]/[ozone] est égal à l'unité.

Cependant, tous nos résultats indiquent clairement un rapport entre l'ozone et l'oxyde d'azote égal à l'unité, bien que certaines de nos expériences ont été effectuées sur des mélanges gazeux identiques à ceux décrits par Zabolotskii.

Dans toutes les expériences décrites ici, la transmission due au bioxyde formé par l'oxygène était maintenue à une valeur aussi élevée que possible de sorte que l'échelle complète de l'enregistreur pouvait être réservée à la mesure de l'effet de l'ozone: des chaînes d'oxydation supérieures à l'unité auraient été très facilement décelées si elles avaient existées dans le système étudié.

De plus, l'exactitude des résultats est démontrée par les oscillations des rapports obtenus autour de l'unité, si légères vis à vis de si vastes limites de concentration du bioxyde d'azote. Finallement, l'accord satisfaisant entre les différentes méthodes de calibration indique la véracité des résultats.

Dans une étude récente sur l'oxydation de l'oxyde d'azote par l'ozone pur à de basses températures, Johnston et Crosby (8) établissent la réaction primaire, bimoléculaire indiquée par l'équation 1.

Dans un excès d'ozone, la réaction secondaire serait naturellement (9).

$$2NO_2 + O_3 \rightarrow N_2O_5 + O_2.$$

Cependant, sous le léger excès d'ozone employé par les auteurs ($[O_3]/[NO_2]$ = 1.1 à 2.2), la réaction secondaire, a été négligée parce que, quoique très rapide, elle était encore beaucoup plus lente que la réaction primaire. Quoiqu'une chaîne de réaction ne pouvait être obtenue dans le système étudié par Johnston et Crosby, à cause de l'absence complète d'oxygène, leurs résultats sont mentionnés pour supporter la réaction de base (1) qui s'applique également dans ce travail. Bien qu'un accord complet ne puisse être invoqué, à cause des conditions expérimentales très différentes, les résultats de Johnston et Crosby (8) soutiennent nos résultats.

SOMMAIRE ET CONCLUSION

L'ozone n'a aucun effet catalytique sur l'oxydation de l'oxyde d'azote par l'oxygène sous les conditions étudiées. Dans de vastes limites de concentrations d'oxyde d'azote, 0.05% à 13%, à la température ambiante et sous la

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pression atmosphérique, nos résultats indiquent clairement la réaction stoïquiométrique entre l'ozone et l'oxyde d'azote telle qu'indiquée par l'équation

$$NO + O_3 \rightarrow NO_2 + O_2.$$

Sous des conditions expérimentales identiques à celles de Zabolotskii il nous fut impossible de reproduire ses résultats.

REMERCIEMENTS

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THE HALF-LIFE OF Ni^{63} [1]

By C. C. McMullen,[2] B. D. Pate,[3,4] R. H. Tomlinson,[2] and L. Yaffe[3]

ABSTRACT

The half-life of Ni^{63} has been found by a specific activity determination to be 125 ± 6 years. The number of atoms of Ni^{63} was determined mass spectrometrically and the disintegration rate by $4\pi\beta$-counting. The cross section for the reaction $Ni^{62}(n, \gamma)Ni^{63}$ has been found to be 21 ± 2 barns, in good agreement with that found by Pomerance.

Ni^{63} is a radionuclide decaying by the emission of negative electrons with a maximum energy of 67 kev. to the ground state of Cu^{63}. The mass assignment has been established by the neutron irradiation of enriched nickel isotopes (1, 2). Various values have been assigned to the half-life of Ni^{63}, each being based on a value of 14.8 barns (9) for the neutron capture cross section of Ni^{62}. Previously published values are given in Table I.

TABLE I

Half-lives assigned to Ni^{63}

Half-life	Determined by
"Several hundred years"	Friedlander (2)
61 years	Wilson (10)
85 years	Brosi *et al.* (1)

Up to this time no attempt had been made to determine the half-life by a specific activity measurement. To do this it is necessary to determine N, the number of atoms of Ni^{63}, and the disintegration rate. Since the disintegration rate, $-dN/dt$, equals $N\lambda$ where λ is the disintegration constant, one can determine the half-life, $t_{\frac{1}{2}}$, from the well-known relationship $\lambda = 0.693/t_{\frac{1}{2}}$.

We have determined N mass spectrometrically and the disintegration rate by an absolute β^- measurement.

EXPERIMENTAL

A. Irradiation

Nickel oxide, enriched in Ni^{62},* was irradiated in a 'tray-rod' position in the center of the NRX nuclear reactor at Chalk River for a period of about three months. The maximum flux in the position used was 5.8×10^{13} neutrons/cm.^{2}/sec. and the integrated flux was $2.15\pm0.20\times10^{20}$ neutrons/cm.^{2}

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B. Mass Spectrometry

(1) Production of Nickel Ions

Various nickel salts were found to be unsuitable for the production of nickel ions by ionization on the surface of a tungsten filament. Nickel metal plated on a tungsten filament also proved unsatisfactory, since this gave ions only at the extremely high filament temperatures which occurred when the filament burnt through.

Success was achieved, however, by plating the nickel out as a 'black' with high surface area on a tungsten filament. The concentration of nickel in the plating solution was about 1 mgm./ml. A platinum anode was used and the nickel was plated out from ammoniacal nickel sulphate solutions at high current densities.

The nickel deposit obtained in this manner gave positive ions at temperatures intermediate to those used for the production of ions from salts of alkali and alkaline earth metals. The positive ion current from a deposit of the nickel black was not observed above the temperature at which the nickel melted.

It is believed that this method of producing positive nickel ions should also prove useful for other elements with high ionization potentials.

(2) Measurement

The measurements were all carried out using a mass spectrometer having a 10 in. radius of curvature and a resolution of one unit at mass 450. The ion current was measured with a 13-stage electron multiplier and vibrating reed electrometer. The shunt factors were calibrated with a potentiometer. About 10 μgm. of nickel were deposited on the filament when the measurement was made. At the temperatures at which the determination was carried out it was found that there was no contribution to the ion currents from the nickel parts in the spectrometer.

C. Disintegration Rate Determination

Since the decay of Ni^{63} takes place by a β^- transition directly to the ground state of Cu^{63} the disintegration rate determination must necessarily be made by measurement of the β^--radiation. This measurement is complicated by the low energies involved and necessitates great care both in source preparation and in measurement.

The method used was 4π-counting and the techniques were those which have been described previously (4, 5, 6, 7, 8).

(1) Preparation and Treatment of Solutions

The short-lived activities in the nickel were allowed to decay away. A portion of the nickel oxide was then dissolved in the minimum quantity of concentrated hydrochloric and nitric acids and the resulting solution made up to a known volume. The nickel concentration of this master solution was then determined colorimetrically using the procedure of Mitchell and Mellon (3).

From the master solution two further solutions were prepared in which the

original nickel concentration was reduced by a factor of 10^2 and 10^3. The determinations of disintegration rates were made from aliquots of these solutions (now called "counting solutions").

(2) Source-mounting

Sources were mounted on accurately calibrated VYNS films (4) coated with about 2 to 5 μgm./cm.^{2} of gold (also accurately determined). Corrections for absorption of radiation in the film were of the order of 2 to 3% and were accurately known (6). Two methods of source preparation were used:

(i) VYNS films were treated with 40 units/cc. insulin solution and rinsed several times with distilled water. Aliquots of the counting solutions were evaporated to dryness on these films. The films were continually rocked to and fro during the evaporation procedure in order to keep all parts of the originally covered area of the film ($\backsim$1 cm.^{2}) wet until the last possible moment. When the amount of solid material in the aliquot used is as small as in the present experiment (10^{-7}–10^{-8} gm. Ni), the macroscopic crystalline deposit described previously (8) is not obtained. In the manner described it is possible to produce even deposits showing one interference color over the whole area in which the active material appears to be uniformly dispersed in the minute amount of insulin remaining.

(ii) The previously described (8) distillation method using nickel dimethylglyoxime was also used. An aliquot from the counting solution was pipetted into the platinum distillation crucible. To this was added an aliquot from a standard inactive nickel solution (to bring the weight of nickel present into the 10^{-5}–10^{-7} gm. range) and the nickel dimethylglyoxime precipitated by the addition of suitable amounts of dimethylglyoxime in alcohol and ammonia. The material was then evaporated to dryness by means of an infrared lamp and the platinum crucible with a calibrated film was transferred to the distillation furnace. Nickel dimethylglyoxime was observed to distill cleanly and quantitatively out of the residue at the temperature and pressure previously (8) determined. Disintegration-rate determinations were made from a series of sources prepared from different sized aliquots of active and inactive nickel solutions.

RESULTS AND DISCUSSION

The abundances of the isotopes in the irradiated and unirradiated enriched nickel are shown in Table II.

TABLE II

PER CENT ABUNDANCES OF NICKEL ISOTOPES IN IRRADIATED AND UNIRRADIATED NICKEL (Enriched in mass 62)

	Mass					
	58	60	61	62	63	64
Unirradiated	1.88±0.12	2.04±0.10	0.29±0.03	95.64±0.23	—	0.15±0.01
Irradiated	1.89±0.13	1.91±0.14	0.28±0.03	95.34±0.25	0.42±0.04	0.16±0.02

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In addition to these results a further series of mass spectrograms was obtained for the irradiated nickel in which only the ratio of Ni^{62}/Ni^{63} was measured. This ratio was found to be 218 ± 10 and was the one used in the calculation of the half-life, i.e. $0.44\pm0.02\%$ Ni^{63}.

The following specific activities were obtained:

(*a*) Insulin-evaporation method—$4.48\pm0.08\times10^5$ disintegrations/minute/microgram of nickel.

(*b*) Distillation of nickel dimethylglyoxime—$4.52\pm0.03\times10^5$ disintegrations/minute/microgram of nickel.

The agreement between the specific activity measurements made by the two different source-mounting techniques is gratifying. It is, however, in disagreement with previous work (8) where it was suggested that a self-absorption of $\backsim6\%$ of the Ni^{63} β^--radiation occurs in the thinnest sources prepared by the distillation method. It would be extremely unlikely that all the sources prepared by the insulin-evaporation technique had a self-absorption of $\backsim6\%$. It appears that the self-absorption effects in both cases are small, and less than the errors quoted. The reason for the constant value of the specific activity found previously (8) over the initial source thickness range is not clear. It may be that a scattering phenomenon, like that in low geometry systems, is responsible.

One can check the expected self-absorption theoretically. Assume as a first approximation that the crystals arising from the distillation are spherical with radius R. If the absorption of the Ni^{63} β^--radiation is taken to be exponential with an absorption coefficient $\mu = 0.87$ cm.^{2}/mgm. (8) it may be shown that the magnitude of the self-absorption (the ratio of the observed specific activity, N_a, to the true specific activity, N_T) is given by

$$\frac{N_a}{N_T} = \frac{1}{\mu R} - \frac{1}{2(\mu R)^2}(1-e^{-2\mu R}) \approx 1-\tfrac{2}{3}(\mu R).$$

The crystals actually found (4) were of the order of 1 μ long and about 0.2 μ in diameter. If one adopts as approximately equivalent a sphere of diameter 0.4 μ, then $R = 0.2$ μ. If the density of the material is approximately unity, then $R = 0.02$ mgm./cm.^{2} From this, one calculates a self-absorption of about 1%, substantiating the above observations.

Half-life Calculation

Specific activity = $(4.50\pm0.05)\times10^5$ dis./min./μgm. Ni.

Contributions to the activity by other nickel isotopes can be neglected. The shorter-lived ones were allowed to decay. Ni^{59}, a nuclide decaying by K-capture with a half-life of 8×10^4 years, contributes a negligible amount ($\backsim10^{-6}$) because of the low abundance of Ni^{58} in the original sample, the low efficiency of the counter for X rays, and the long half-life of Ni^{59}.

Atomic weight of unirradiated enriched nickel = 61.82.

Abundance of Ni^{63} relative to Ni^{62} = 0.44 ± 0.02.

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Therefore, since λN = disintegration rate

$$\frac{6.02\times10^{23}}{61.82}\times10^{-6}\times0.44\times10^{-2}\times\frac{0.693}{t_{\frac{1}{2}}} = 4.50\times10^{5},$$

and

$$t_{\frac{1}{2}} = 65404 \text{ minutes}$$
$$= 125\pm6 \text{ years.}$$

Cross Section for The Reaction $Ni^{62}(n, \gamma)Ni^{63}$

Since the half-life of Ni^{63} is long compared to the time between irradiation and mass spectrometric analysis, then

$$N_{63} = N_{62}\,\sigma(nv)t$$

where N_{62}/N_{63}, the ratio of the number of Ni^{62} to Ni^{63} atoms, is 218 ± 10,

$(nv)t$, the integrated flux, is $2.15\pm0.20\times10^{20}$ neutrons/cm.^{2},

and σ is the neutron cross section for the reaction $Ni^{62}(n, \gamma)Ni^{63}$,

whence $\sigma = 21\pm2$ barns.

This is the cross section for pile neutrons and agrees quite well with Pomerance's (9) value of 14.8 barns. If one bases the half-life value obtained by Brosi *et al.* (1) on our cross section value, they obtain 120 years for the half-life of Ni^{63}, in excellent agreement with our value.

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EXTRACTION OF A LIGNIN FRACTION FROM MAPLE WOOD BY LIQUID AMMONIA[1]

By M. M. Yan[2] and C. B. Purves

ABSTRACT

Solvent-extracted maple wood meal when re-extracted with nearly anhydrous liquid ammonia at room temperature (about 150 p.s.i.) lost most of its acetyl groups as 4% of acetamide, 0.9% of a polyuronide, and about 1% of lignin. When fractionated, the latter yielded half its weight as subfractions that were nearly uniform in composition and whose cryoscopic molecular weights in dioxane were all near 1000. If the sample was indeed homogeneous, the corresponding molecular formula, $C_{42}H_{38}O_{10}(OH)_5(OCH_3)_7$, suggested that this fraction was chemically less condensed than the bulk of the lignin in the wood. The behavior of the fraction toward methanolysis, toward oxidation with periodate, and in a sulphite cook is described.

INTRODUCTION

As noted in a previous article (17), 99.5% liquid ammonia could extract up to 14% by weight of a hardwood meal, and the extract could include up to 30% of the lignin. Since the chemical action of nearly anhydrous liquid ammonia was expected to be mild, and the yield of extract was substantial, it seemed desirable to study the action of liquid ammonia upon a hardwood in greater detail. Maple wood flour, thoroughly freed from soluble materials by extractions with alcohol–benzene and with water, was chosen for this purpose.

Although preliminary experiments showed that extraction with liquid ammonia was more effective at 100°, or even at 45°, a temperature of 25° was adopted in order to minimize the risk of chemical change. Since the extraction proceeded rapidly for the first few hours, and very slowly thereafter, the time of extraction could be limited to five hours. An apparatus was built in which 1 kgm. of the wood meal could be conveniently treated with 5 kgm. of anhydrous liquid ammonia at 25° near 150 p.s.i., and the extract separated and evaporated, all without access of atmospheric moisture. As Fig. 1 shows, the amber-colored extract yielded: a crude polysaccharide, which was not examined in detail, but which was probably a pectin; a pure, crystalline acetamide amounting to at least two-thirds of the acetyl groups originally in the wood; and various crude lignin fractions which differed in their solubility and Klason lignin content (74.0, 90.2, and 84.5% for Fractions II, IV, and IV*a*, respectively). The yield of acetamide corresponded to 2.92% as acetyl groups, and with this correction the recovery of the total extract was about 88% of the loss in weight of the wood. Although Bishop (2) described the isolation of a polyuronide, of acetamide, and of a lignin fraction from a liquid ammonia extract of wheat straw holocellulose, the present appears to be the first occasion when similar observations were made on a whole wood meal.

[1]*Manuscript received July 30, 1956.*
Contribution from the Division of Industrial and Cellulose Chemistry, McGill University, and the Wood Chemistry Division, Pulp and Paper Research Institute of Canada, Montreal, Que. Abstracted from a Ph.D. thesis submitted to the University by M.M.Y. in September, 1947.
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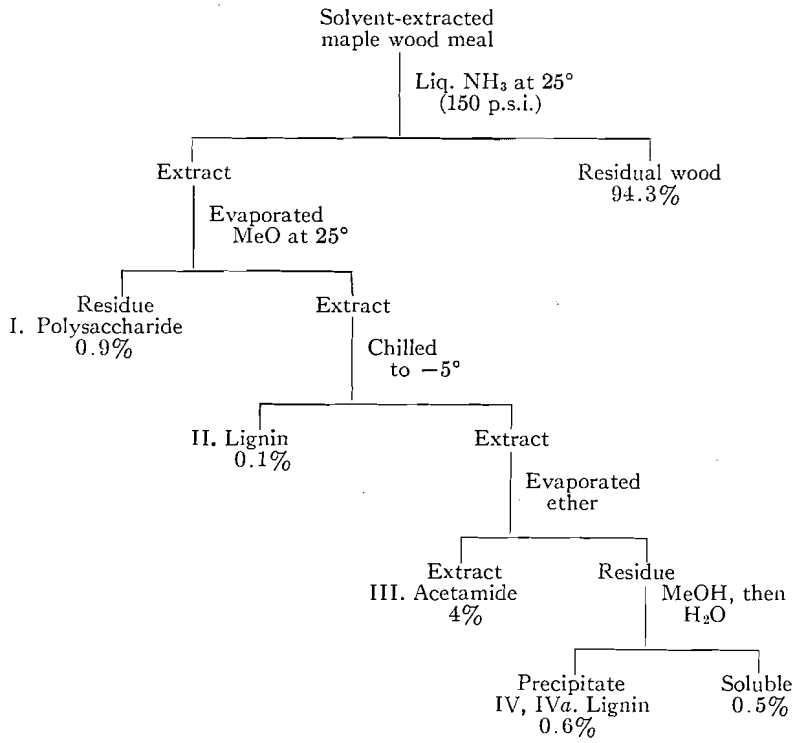

FIG. 1. Extraction of maple wood meal with liquid ammonia. All percentages based on original wood.

The crude lignin Fractions IV and IV*a*, which differed mainly in physical state, were each separated into three portions by a tedious series of extractions and precipitations, the relative amounts of these portions differing in the two cases. The first portions, insoluble in both dioxane and methanol, gave a weak response in the Mäule (15) test for angiosperm (syringyl) lignin, and no red-violet color in the phloroglucinol – hydrochloric acid test (4) for lignins in general. The resinous, impervious character of these portions was sufficient to make them dissolve only very slowly in cold 1% sodium hydroxide, pyridine, or glacial acetic acid, and might have interfered in the above tests. Both the second portion, soluble in dioxane but not in methanol, and the third portion, soluble in both these liquids, were intensely positive in the Mäule test, but their response in the phloroglucinol test was only moderate. All fractions could be precipitated by carbon dioxide from their solutions in dilute aqueous alkali, and presumably contained free phenolic, but not carboxylic acid, groups.

About half of the lignin extracted by the ammonia, corresponding to about 3% of the original Klason lignin, was isolated as a very light colored powder, free of nitrogen, soluble in methanol, and easily soluble in cold, anhydrous dioxane to give a clear solution. This solution was optically inactive within the limits of observational error, a result which confirmed an earlier observation of the optical inactivity of lignin (9) which had to be made with greater uncertainty. A solution of the methanol-soluble Fraction IV on fractional

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reprecipitation yielded the subfractions IV–1 to IV–4, and the compositions of the last three subfractions were practically the same (Table I). Throughout the work, care had been taken to avoid the use of mineral acids and alkalies, and all evaporation and drying had been carried out under diminished pressure at not more than 60°. Adventitious changes in any of the wood constituents were therefore near the minimum. These circumstances suggested that it would be worth while to determine the molecular weights of the lignin fractions provided the method used did not involve an elevated temperature. Cryoscopy in pure dioxane was chosen, and was previously used by Payne and his collaborators (12) to determine the molecular weight of a lignin from bagasse as 1490–1860. As Table I shows, the observed values supported the assumption that the lignin Fraction IV was nearly homogeneous; these values were reproducible, and were thought to be reliable to within ±125 units.

The assumption that subfractions IV–2 to IV–4 consisted of a single chemical individual led to the molecular formula $C_{42}H_{43}O_{15}(OCH_3)_7$. When the analyses found by Kudzin and Nord (11) for a maple "native" lignin were calculated to a C_{42} skeleton, the empirical formula was $C_{42}H_{37}O_{14}(OCH_3)_{5.2}$, and those for maple periodate lignin (13) corresponded to $C_{42}H_{34.2}O_{16}(OCH_3)_{6.6}$. The liquid ammonia lignin was obviously in a less oxidized or condensed condition than the other two. In accord with this inference, boiling methanolic hydrogen chloride changed almost half of the ammonia lignin to water-soluble substances, and only 53% was recovered as the water-insoluble methanol lignin. Brauns (3) found that the yield of methanol lignin from spruce "native" lignin was nearly quantitative. He also showed that his spruce "native" lignin

TABLE I

COMPOSITION OF LIGNIN FRACTIONS SOLUBLE BOTH IN METHANOL AND DIOXANE

Fraction	Yield,[a] %	Analyses[b]			Mol. wt.[c]
		C, %	H, %	OCH_3, %	
IV*a*	—	—	—	20.7	840
IV	—	58.9	6.5	21.6	1130, 1050
IV–1	6	57.9	6.7	19.4	—
IV–2	29	57.9	6.4	21.6	900, 1350[d]
IV–3	46	58.2	6.4	21.6	1140
IV–4	15	58.5	6.4	21.8	1010
Native[e]	—	61.0	5.6	17.4	—
Periodate[f]	—	58.4	5.4	20.4	—

[a]*By fractionally precipitating a 4.5% dioxane solution of IV with ether. Total yield 96%.*
[b]*Mean of concordant duplicate or triplicate determinations. Calc. for* $C_{42}H_{43}O_{15}(OCH_3)_7$*: C, 58.5; H, 6.4; OCH₃, 21.6; mol. wt., 1004.*
[c]*From freezing point of dioxane solutions.*
[d]*Value of 1350 observed after reprecipitation from dioxane–ether in almost 100% yield and unchanged methoxyl content, and drying for one week* in vacuo *at 55°.*
[e]*Extracted with neutral ethanol by Kudzin and Nord (Ref. 11).*
[f]*Ritchie and Purves (Ref. 13). Lignin insoluble in methanol and dioxane.*

dissolved almost completely in a standard sulphite cook, but only 39% of the present maple ammonia lignin dissolved when heated for six hours at 130° in a calcium bisulphite solution containing 1% of combined and 4.7% of total sulphur dioxide. The undissolved portion was sulphonated. Since 17% of

the maple ammonia lignin was soluble in 20% aqueous sodium bisulphite at room temperature, it seemed probable that the temperature of the cook condensed this sample more rapidly than sulphonation promoted its solution (5).

The formula of Fraction IV could be expanded to $C_{42}H_{38}O_{10}(OH)_5(OCH_3)_7$ because methylation with dimethyl sulphate and alkali introduced five additional methyl ether groups per mole; Wright and Hibbert (16), however, found that this procedure tended to give slightly too high an estimate. A portion of Fraction IV was alternately oxidized with aqueous sodium periodate at 20° and extracted with boiling water, as in the isolation of periodate lignin from maple wood (13). The moles of periodate reduced per mole of the lignin fraction depended on the experimental conditions, and no definite integral number could be discovered. Adler and Hernestam (1) recently showed that free phenols, as well as 1,2-glycols, reduced aqueous periodate, and in consequence the results of the present experiments could not be interpreted. No less than 39% of Fraction IV dissolved during two oxidation cycles, and 48% after three, whereas only 25% of the lignin was lost during isolation from the wood by five similar oxidations (13). This easy oxidizability by periodate, together with the solubility of the ammonia lignin in several liquids, showed that the fraction was not representative of the bulk of the lignin in the maple wood. The absence of chemical change during the extraction of the fraction also remained unproved.

EXPERIMENTAL

Mr. A. J. Philip of the Canada Paper Company, Windsor Mills, Quebec, kindly supplied a newly cut log of sugar maple (*Acer saccharum* Marsh) from a tree about 90 years old and 9 in. thick, 4 in. of which was heartwood. The log was chipped and then ground in a Wiley mill, the portion of 40 to 80 mesh size amounting to 65 to 73% by weight. This portion was then exhaustively extracted in a large Soxhlet apparatus first with hot ethanol–benzene for 72 hr., then with hot ethanol for 48 hr., then with running tap water at 55° for 48 hr., and finally with distilled water for four hours. The meal was dried in the air, and further dried at 50° *in vacuo* for three days.

Small, 3.33 gm., samples of the wood meal were then extracted at 25° with 50 gm. of anhydrous liquid ammonia, exactly as described previously (17). After extractions lasting 1, 5, 24, 48, and 96 hr., 2.8, 5.6, 5.5, 5.6, and 6.0% respectively of the wood had gone into solution. Another sample of maple wood lost 6.4, 6.9% by weight when extracted for 110 hr. at 25° and 45°, respectively. When extracted at 100° for 24 hr. a 60–80 mesh sample of the wood meal lost 8.9% by weight, and this loss was increased to only 10.6% for a sample ground to 140–180 mesh size.

Extractions with Liquid Ammonia (Fig. 1)

A bomb of 11 liters capacity was made from a heavy, stainless steel pipe 48 in. long and 6.5 in. in diameter, which was sealed at one end and threaded on the outside of the open end. This thread engaged a similar thread on the

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inside of a heavy top. Eight bolts could be screwed through the top to press a separate heavy lid carrying a lead gasket against the open aperture of the bomb. This lid was pierced by an inlet and an outlet tube whose inner ends were both protected from the wood meal by disks of 60-mesh steel screen, and whose outer ends carried 0.25 in. steel needle valves. The bomb, charged with 1 kgm. of the dry wood meal, was chilled to about $-10°$ and set on a suitable platform-scale. The inlet valve was connected to a cylinder of commercial 99.9% ammonia arranged to deliver the liquid, and the outlet valve led through heavy rubber tubing to an efficient fume hood. After the bomb was weighed to the nearest 120 gm., both valves were opened and the liquid ammonia was allowed to run in slowly. At first, a rush of gaseous ammonia escaped because the bomb and its contents were insufficiently cooled, and because the heat of dilution of the residual moisture in the wood by the ammonia was considerable. In later experiments with bark containing about 10% of water, this effect raised the external temperature of the bomb in local patches to more than 30°. The rate of addition of the liquid ammonia could soon be increased, and 5 ± 0.25 kgm. could be added within an hour. This amount was sufficient to cover the wood meal completely and to reduce the over-all moisture content to about 0.3%. The valve on the cylinder, the inlet valve, and the outlet valve were then closed in that order, the bomb was brought near room temperature by a brief immersion in warm water, and was rocked for five hours near 25° in a motor-driven carriage.

After five hours, the bomb was held in an inverted position, and the outlet tube was connected by thick-walled rubber tubing to a 12 liter Pyrex flask carrying a rubber stopper fitted with glass inlet and outlet tubes. The inlet tube projected several inches into the flask, while the shorter outlet tube led to the fume hood. When the exit valve on the bomb was carefully opened, the liquid ammonia was forced into the flask, the flow being kept slow enough to avoid blowing some of the extract out of the receiver. Although the flow ceased in about 15 min., about one-fourth of the ammonia remained in the bomb. To remove this fraction, another 2.5 kgm. of liquid ammonia was added to the bomb, which was sealed and shaken for 30 min. before being discharged in the same way. This washing procedure was repeated once. The wood meal was then recovered, allowed to stand in the air until nearly free from the odor of ammonia, and was stored in a closed container (see below). The inlet and outlet tubes of the flask containing the extract and washings were protected against atmospheric moisture by tubes containing solid sodium hydroxide, and the liquid ammonia was allowed to distill away at atmospheric pressure. This process was complete within 24 hr., and the flask was then ready to receive the extract from another kilogram of the wood meal.

A total of 3085 gm., on a bone dry basis, of wood meal lost 175.5 gm. (5.7%) in weight during the extraction, but the extract weighed 210 gm. (6.8%) after being dried at 50° *in vacuo*. The discrepancy arose from the retention of the amino group in the acetamide. One kilogram of the recovered wood meal was re-extracted for 25 hr. near 25° with 5 kgm. of the liquid ammonia. The extract yielded 0.54% of the wood as a dark-brown, brittle resin which

was insoluble in dioxane. Found: Klason lignin, 71.5, 72.9; OCH_3, 19.1, 19.2; N, 0.73%. The total loss in weight of the wood meal was therefore 5.7+0.54%, or about 6.2%. A duplicate extraction of a second 3 kgm. batch of the wood meal by Neubauer yielded 189 gm., or 6.3%, of isolated extract.

Isolation of a Crude Polysaccharide (*Fig. 1*)

The 210 gm. of the dry extract, a red-brown semisolid resin studded with crystals, was dispersed by vigorous stirring in 6 liters of methanol, and the finely divided, light-brown material (Fraction I) which failed to dissolve was removed on a sintered glass suction filter. The filtrate, when diluted with 4 liters of methanol and kept at −5°, deposited a small additional amount of the flocculent material, which was easily separated by decantation from a deposit of a brittle, darker resin, 3.5 gm. (Fraction II) and was added to Fraction I. Fractions I and II were separately and thoroughly washed with methanol, all methanol filtrates and washings being combined and saved. Found for Fraction II: Klason lignin, 74.0; OCH_3, 20.3; N, 0.64%. This fraction consisted essentially of lignin which was very sparingly soluble in methanol, but which dissolved slowly and completely in 1% sodium hydroxide. Acidification of the latter solution precipitated most of the material, 5% of which was soluble in methanol, 26% in dioxane but not in methanol, and 65% insoluble in methanol and dioxane (see below).

Fraction I, 26.9 gm., amounted to 0.9% of the wood, but the yield in a duplicate extraction by Neubauer was 1.2%. This fraction was insoluble in water, toluene, ethyl acetate, carbon tetrachloride, and dioxane, either cold or boiling, but was partly soluble in pyridine. A 0.66 gm. sample was accordingly extracted with six 30 cc. volumes of cold pyridine, and the undissolved portion was washed with 300 cc. of ether. When the pyridine and ether extracts were combined, a yellow curd separated, which was recovered, extracted with a little ether, and dried *in vacuo*. This curd, yield 0.105 gm. or 16% of Fraction I, consisted mainly of lignin. Found: C, 54.9; H, 6.4; OCH_3, 16.2, 16.2%. The portion insoluble in pyridine, about 0.55 gm. of a light-brown powder, was also dried to constant weight *in vacuo*. Found: C, 43.7, 43.8; H, 7.0, 6.8; OCH_3, 4.3, 4.5; pentosan, 7.8, 5.9; Klason lignin, 18.0%. A small sample, when sprayed in succession with aqueous potassium permanganate, hydrochloric acid, and ammonia, gave a feeble coloration in the Mäule reaction (15) for angiosperm lignin. When the carbon and methoxy content of the sample was corrected for the presence of 18% of lignin, the results were close to the values C, 40.9; OCH_3, 0%, required by a polyuronide. The easy solubility of the sample in cold dilute alkali, and complete reprecipitation when the solution was acidified, were also characteristic of a polyuronide.

Isolation of Acetamide (*Fig. 1*)

The combined methanol liquors were evaporated under diminished pressure, and the oily residue was extracted for 30 min. under reflux with boiling ether. Acetamide (Fraction III) crystallized when the extract was chilled to −15° and was recovered. The mother liquor was then used to re-extract the residue.

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After a dozen such extractions, the recovery of acetamide was 123.5 gm. (4.0%) with a melting point of 80.5° (corr.), undepressed by admixture with an authentic sample melting correctly at 81° (corr.). Found: N, 23.5%. Calc. for CH_3CONH_2: N, 23.5%.

Isolation of Lignin (*Fig. 1*)

The gummy residue from the extractions with ether was dissolved with some difficulty in 1 liter of methanol; the solution was filtered and was stirred into 5 liters of water to precipitate Fraction IV, a yellow powder. A brown oil which soon hardened to a crust (Fraction IV*a*) floated on the supernatant liquor and was easily removed. Yield 4.0 gm. after thorough washing with water and drying. Found: Klason lignin, 84.5; OCH_3, 20.9; N, 0.58%. Evaporation of the combined aqueous liquors under diminished pressure caused the separation of a little more of Fraction IV, and further evaporation of the filtrate left a dark-brown, semicrystalline residue weighing 16 gm. and containing acetamide.

A 6 gm. sample of Fraction IV was extracted five times during 72 hr. with a total of 275 cc. of methanol at room temperature, after which the rate of solution was exceedingly slow. The residue, 1.36 gm. or 22.6%, was lignin. After a few hours, a small amount of brown resin separated from the amber-colored extracts, which were then clear. Each extract was separately diluted with two volumes of water, and some of the lignin separated as a faintly yellow suspension; about one-third, however, separated as a slightly darker, coherent resin which was readily collected. The two portions were thoroughly washed with water and dried *in vacuo* at 55°. Combined yield, 3.54 gm. or 59%. Both portions dissolved quickly and completely in peroxide-free, anhydrous dioxane and the resulting 1% solutions had the same depth of color. Both solutions were accordingly combined and filtered to remove a trace of insoluble material. When the mixture was poured into three volumes of rapidly stirred, absolute diethyl ether, a very finely divided, buff precipitate separated and was removed on the centrifuge. It was important to avoid loss of ether by evaporation from the moist precipitate, because the residual dioxane quickly converted the product to an inconvenient gum. The moist precipitate was quickly solvent-exchanged through diethyl ether into low-boiling ligroin, and was dried for 24 hr. *in vacuo* at 55°. Yield 3.0 gm. or 50% of the crude Fraction IV. Found: N, 0.0%. The optical rotation in sodium light of a 2.4% solution of the purified fraction in dioxane was −0.03°, or zero within the observational error in a 1 dm. tube. A further 11.7% of Fraction IV was insoluble in methanol but soluble in dioxane, while 6.8% was insoluble in both these liquids. Fraction IV*a* when examined in substantially the same way yielded 49% soluble in both methanol and dioxane, 26.4% insoluble in methanol and soluble in dioxane, and 5.7% insoluble in both liquids. Table I contains the analyses of the most soluble fractions.

A 2.05 gm. sample of the methanol-soluble, dioxane-soluble Fraction IV was fractionally precipitated by solution in 45 cc. of pure dioxane contained in a 200 cc. centrifuge cup. Purified chilled diethyl ether, 7 cc., was added

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drop by drop to precipitate Fraction IV–1; additions of 9 cc. and of about 15 cc. caused the precipitation of Fractions IV–2 and IV–3, and Fraction IV–4 was obtained by flooding the mother liquor with ether. Each fraction was reprecipitated from solution in 60 cc. of dioxane by the addition of two volumes of ether, was thoroughly washed in ether and ligroin, and was dried *in vacuo* at 50°. All were light-colored, highly electrostatic powders (Table I).

The Beckmann technique described by Findlay (7) was used to determine the cyroscopic molecular weights of the lignin fractions in dioxane (Table I). Eigenberger's method (6) was used to free the dioxane from any acetals, and after being distilled over sodium the product was stored under nitrogen in the dark. In order to obtain reproducible freezing points, it was essential to exclude atmospheric moisture (14) by continuously sweeping the Beckmann apparatus with dry nitrogen introduced through the side-arm. The gas usually volatilized 0.5 to 1 gm. of the dioxane, and the exact weight present was found by weighing the assembly at the beginning and end of each determination. Using 0.1–0.25 gm. samples of pure naphthalene in about 15 gm. of the dioxane, the molecular freezing point constant was determined as 4.66°, 4.65°, and 4.64°, the value established by the careful work of Kraus and Vingee (10) being 4.63°. The lignin samples weighed 0.3–0.6 gm., and successive determinations of the freezing point of a given solution did not alter the observed depressions of 0.11° to 0.22° by more than 0.002°.

Some Reactions of Lignin Fraction IV

The methylation of 0.60 gm. of the fraction was accomplished by solution in 35 cc. of dioxane, followed by the simultaneous addition, with stirring, of 12 cc. of 35% aqueous sodium hydroxide and of 8 cc. of dimethyl sulphate. Two hours later, the emulsion was boiled for 30 min., was acidified, and was poured into 500 cc. of water. The dioxane was replaced by 1% sodium hydroxide in the subsequent five methylations, after which the methoxyl content of the light colored product ceased to increase. Yield, 0.41 gm. Found: C, 61.0, 61.1; H, 7.0, 6.9; OCH_3, 34.6, 34.8%. Calc. for $C_{42}H_{38}O_{10}(OCH_3)_{12}$: C, 60.3; H, 6.9; OCH_3, 34.6%.

A 0.32 gm. sample of Fraction IV was methanolyzed by being heated under reflux for 48 hr. with 25 cc. of 2% methanolic hydrogen chloride. Access of moisture was prevented and a nitrogen atmosphere was maintained. All but 1.9% of the sample was dissolved; the clear filtrate was neutralized with sodium carbonate and poured with stirring into 400 cc. of water. After being washed and then dried *in vacuo*, the chocolate-colored precipitate of methanol lignin weighed 0.17 gm., the yield being 53%. Found: OCH_3, 28.4, 28.8%.

Aqueous 4% sodium periodate, 2 cc., buffered to pH 4 with acetic acid, was used to oxidize 0.06 to 0.10 gm. samples of the lignin Fraction IV at 25°. The residual periodate was determined at intervals by the arsenite method of Fleury and Lange (8), and a molecular weight of 1004 was accepted for the lignin. After 2, 24, and 72 hr., the moles of periodate reduced per mole were 1.2, 2.1, and 3.2, respectively. The residual lignin was boiled under reflux for three hours in water, as in the isolation of periodate lignin, and was then

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dried. Yield 64%. In another experiment, the same sample of lignin was oxidized with 2.4% sodium periodate for successive periods of 60 hr., 1.2, 2.0, and 2.7 moles being reduced after 60, 120, and 180 hr., respectively. Only 61% and 52% of the lignin remained undissolved after the second and third oxidations.

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THE OH STRETCHING FREQUENCIES OF SOME NEW ALCOHOLS[1]

By F. A. L. Anet and P. M. G. Bavin[2]

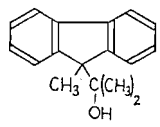
ABSTRACT

The OH stretching frequencies of some new alcohols have been measured in dilute carbon disulphide solution. The frequency shifts from the values observed for simple alcohols are interpreted in terms of hydrogen bonding, steric hindrance, and interaction of the OH group with π-electron systems.

The frequencies associated with the stretching vibration of the hydroxyl group have been measured for some new alcohols, at concentrations low enough to eliminate the effects of intermolecular hydrogen bonding (5).

For simple alcohols, we found the following: *primary*, 3636 cm.$^{-1}$ (methanol to dodecyl alcohol); *secondary*, 3623 cm.$^{-1}$ (isopropanol and *s*-butanol); *tertiary*, 3615 cm.$^{-1}$ (*t*-butanol) and 3616 cm.$^{-1}$ (*t*-pentanol). These values are in excellent agreement with those reported in the literature (see (3) and (5)), their measurement having served to check the calibration of the instrument and to justify the method used.

The alcohol (I), 2-(9-methyl-9-fluorenyl)-propan-2-ol, has a stretching frequency of 3615 cm.$^{-1}$, expected for a tertiary alcohol. The value for tri-*t*-butyl carbinol (3628 cm.$^{-1}$) requires the OH bond to be stronger than for the simple tertiary alcohols, possibly owing to the very strong steric effects of the *t*-butyl groups weakening the CO bond and hence strengthening the OH bond.



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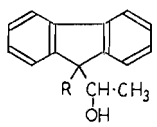

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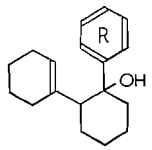

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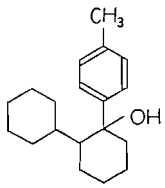

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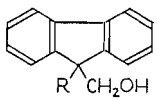

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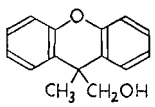

VII

The alcohols (II) have frequencies close to those of simple secondary alcohols (see Table I).

The tertiary alcohols (III) have abnormally low stretching frequencies, around 3545 cm.$^{-1}$ (see Table II) (cf. benzyl alcohol, 3614 cm.$^{-1}$, and tri-

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Contribution from the Department of Chemistry, University of Ottawa, Ottawa, Ontario.
[2]*National Research Council Postdoctorate Fellow, 1954–1956.*

TABLE I

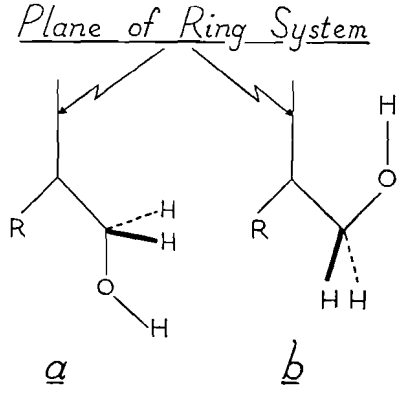
R	Frequency, cm.$^{-1}$ (V)	Frequency, cm.$^{-1}$ (II)
Benzyl	3629	
Hydrogen	3627	
Methyl	3627	3620
Ethyl	3625	
Isopropyl	3625 3598	
t-Pentyl	3596	
t-Butyl	3594	3618

TABLE II

R	Frequency, cm.$^{-1}$
Phenyl	3549
p-Tolyl	3549
p-Fluorophenyl	3548
o-Tolyl	3544

phenylcarbinol, 3606 cm.$^{-1}$), apparently owing to the proximity of the OH group and the ethylenic π-electrons. π-Bonding of a similar nature has been postulated previously in connection with other problems (4 and references given there). This view is supported by the spectrum of 1-(*p*-tolyl)-2-cyclohexylcyclohexanol (IV), which shows a doublet at 3601 and 3623 cm.$^{-1}$ in the region expected for an α-phenyl *t*-carbinol. The doublet may be due to the presence of conformational isomers.

The alcohols of type (V) offer a more complex problem. Examination of the data in Table I shows that they fall into two groups about the isopropyl derivative, the spectrum of which shows a doublet. The peaks of the doublet correspond to those of the two groups.



It appears that when R is isopropyl in (V), rotational isomers of type (VI*b*) become important for the first time. In (VI*b*), the OH group is in the field of

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the aromatic π-electrons, interaction with which will weaken the OH bond, as with the alcohols of type (III). On this basis, the methyl, ethyl, and benzyl derivatives exist largely as (VI*a*), the *t*-butyl and *t*-pentyl compounds existing mostly as (VI*b*). Since the isopropyl is the only compound to show a doublet, it seems likely to consist of (VI*a*) and (VI*b*) in approximately equal amounts.

Measurement of the isopropyl derivative's spectrum at low temperature showed that it was strongly temperature-dependent, the intensity being trebled. The low frequency peak, attributed to (VI*b*, R is isopropyl), then had almost the same intensity as the other, instead of approximately one half.

The related alcohol (VII), 9-methyl-9-hydroxymethylxanthene, has a stretching frequency of 3597 cm.$^{-1}$, comparable with that of tetrahydrofurfuryl alcohol (3594 cm.$^{-1}$). The low frequency is probably due to weak intramolecular hydrogen bonding with the ether function.

Our results show that it is not possible to differentiate between primary, secondary, and tertiary alcohols from measurements of the OH stretching frequencies, in agreement with other workers. (See (3) and (5).)

EXPERIMENTAL

The preparation of the xanthene and fluorene alcohols is described elsewhere (1). Preparations of the 1-aryl-2-cyclohexenylcyclohexanols are taken from the literature (2, 6). They were distilled at 0.01 mm. to limit decomposition, but the *o*-tolyl derivative was still badly discolored.

The sample of tri-*t*-butyl carbinol was generously provided by Professor Paul Bartlett to whom we offer our thanks.

Other samples of alcohols were the purest obtainable.

1-(p-Tolyl)-2-cyclohexylcyclohexanol

The cyclohexenyl compound ((III), R is *p*-tolyl) readily absorbed 1.1 moles of hydrogen when hydrogenated at atmospheric pressure, using 5% palladium on charcoal as catalyst and hexane as solvent. The catalyst was removed by filtration through Celite. Concentration of the filtrate gave prisms, recrystallized from hexane, m.p. 93–95° (84%).

The ultraviolet spectrum in ethanol showed a typical *p*-xylene spectrum with maxima at 273, 266.5, 264.5, 258.8, and 252.5 mμ.

The course of the hydrogenation was easily followed in the infrared region. A suitable aliquot was removed, filtered, and evaporated, and the infrared spectrum of the residue measured in carbon disulphide solution. A typical curve is shown in Fig. 1, in which the reaction is almost complete.

Measurements

The spectra were measured in carbon disulphide solution using a Beckman DK-2 Self-recording Spectrophotometer. Solutions were 0.001 to 0.01 *M* with a 1 cm. light path, giving absorbance readings of 10–40%.

The low temperature experiment was performed as follows: the end of a large centrifuge tube was placed in the sample cell so as not to interfere with the light path. The tube dipped into the liquid, which was cooled by slowly

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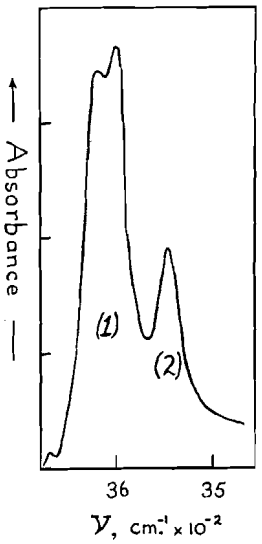

FIG. 1. (*1*) 1-(*p*-Tolyl)-2-cyclohexylcyclohexanol. (*2*) 1-(*p*-Tolyl)-2-cyclohexenylcyclohexanol.

dripping liquid nitrogen into the centrifuge tube. Moisture was excluded from the sample by a cotton wool plug. Frosting of the cell in the light path was prevented by suitably directed jets of dry nitrogen.

When it was judged that the sample had been cooled sufficiently, addition of liquid nitrogen was stopped. Steadiness of the recorder pen indicated thermal equilibrium, and the spectrum was then taken.

A blank experiment showed that the transparency of carbon disulphide was unaltered at low temperatures. Measurement of the temperatures produced was not possible.

ACKNOWLEDGMENT

The authors are grateful to Dr. Camille Sandorfy of the University of Montreal for helpful criticism of the manuscript.

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THE POLAROGRAPHY OF THE METHYL DERIVATIVES OF MALEIC HYDRAZIDE AND EXPLANATION OF THE MALEIC HYDRAZIDE WAVES[1]

By D. M. Miller

ABSTRACT

Maleic hydrazide was previously reported to have two sets of pH dependent double waves, one at low pH for which existing theories provide adequate explanation and one at higher pH for which no explanation has been offered to date. The present work is an attempt to discover the reasons for the existence of the second set of waves. An investigation of several methyl derivatives of maleic hydrazide failed to provide the desired explanation; however, a mechanism which gives a good qualitative and approximately quantitative expression for the dependence of diffusion currents and half wave potentials on pH is offered. This theory is based on the fact that succinic hydrazide, a probable product of the reduction of maleic hydrazide, has been found to have a pK_a of 8.10 and thus to be present in both ionized and unionized forms over the pH range for which the double waves occur.

In an earlier publication (4) maleic hydrazide (MH) was shown to exhibit three pH dependent polarographic waves (see MH, Fig. 1). Below pH 4 a single wave (I) occurs but as the pH is increased this wave diminishes in height and is replaced by a second wave (II) occurring at more negative potentials. The sum of the two wave heights remains approximately constant so that the increment in II equals the drop in I. At pH 5.9 the two waves are equal while at pH 7 wave I is completely replaced by II, which is at its maximum height. Beyond pH 7 wave II falls off with the appearance of a third wave, III, whose height increases at the same rate as that of II decreases. These two waves were reported to be equal at pH 8.2. Polarographically, then, MH produces two sets of double waves over two different pH ranges. These waves will be referred to hereafter as I and IIA for the first set and IIB and III for the second.

It has been shown (5) that MH is a monobasic acid with a pK_a of 5.65, so that over the pH range in which the first set of double waves occur, both the dissociated and undissociated forms of the acid exist, and the theory of Wiesner and others applies. (For a review of this theory see for example 1, 3, 6.) According to this treatment wave I results from the reduction of the undissociated acid, either directly, at low pH, or following the association of the anion with hydrogen ion, at higher pH. With decreasing hydrogen ion concentration the association reaction becomes slower, the wave height is then limited by the rate of the association process rather than diffusion, and is said to be kinetically controlled.

The Ilkovic equation predicts that the diffusion current of a wave varies as the half power of the dropping mercury electrode reservoir height. Since this applies only to a diffusion limited wave, kinetic waves do not show this relationship and this fact is used to distinguish between the two types of waves.

[1]*Manuscript received August 23, 1956.*
Contribution No. 86, Science Service Laboratory, Canada Department of Agriculture, University Sub Post Office, London, Ontario.

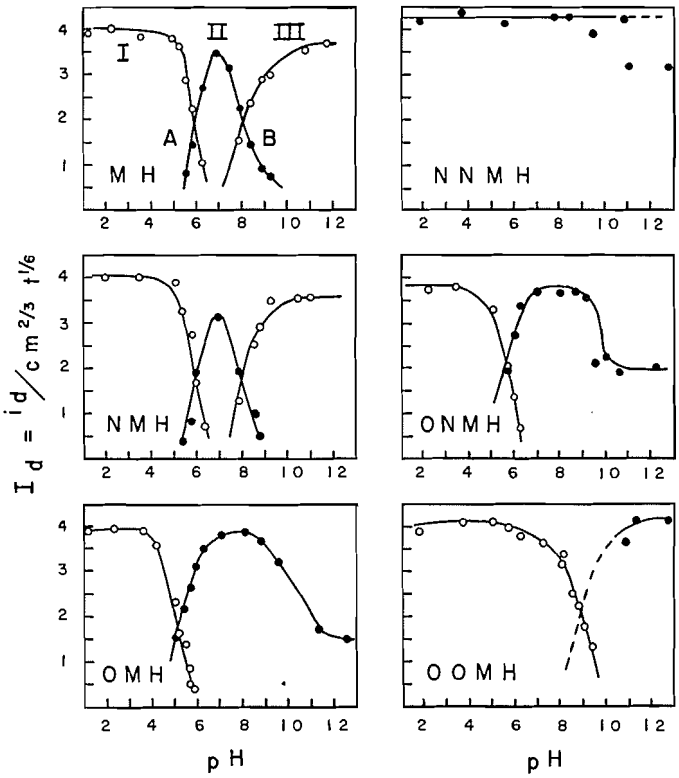


FIG. 1. Half wave potentials as a function of pH for MH and some of its methyl derivatives.

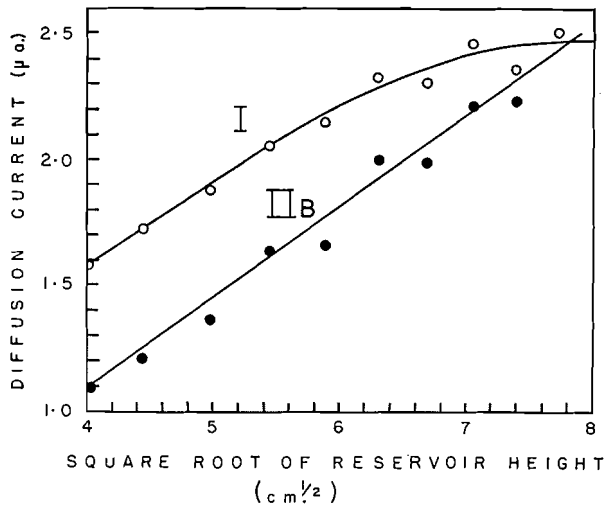


FIG. 2. Dependence of diffusion current on wave height for waves I and IIB.

Fig. 2 is a plot of diffusion current against the square root of the reservoir height for waves I and IIB. The kinetic nature of wave I is amply demonstrated by its deviation from a straight line. Wave IIB on the other hand shows no such deviation but follows the Ilkovic relationship indicating that

it is diffusion controlled. An alternate explanation, therefore, is required for waves IIB and III, and it was in the hope of obtaining such an explanation that the present investigation of the polarography of the methyl derivatives of MH was undertaken.

EXPERIMENTAL

The methyl derivatives used in this work were the following:

N-methyl maleic hydrazide (NMH) (2-methyl-6-hydroxy-3(2H)pyridazinone),

O-methyl maleic hydrazide (OMH) (6-methoxy-3(2H)pyridazinone),

N,N′-dimethyl maleic hydrazide (NNMH) (1,2-dimethyl-3,6-(1H,2H)-pyridazinedione),

ON-dimethyl maleic hydrazide (ONMH) (2-methyl-6-methoxy-3(2H)-pyridazinone),

OO′-dimethyl maleic hydrazide (OOMH) (3,6-dimethoxypyridazine).

The preparation of these compounds has already been reported (5). Polarograms were made on the methyl derivatives in the same way as on MH (4) with the exception that $Na_4P_2O_7$ buffer was used in the pH range 5 to 9. The polarographic constants (I_d) and half wave potentials were obtained from each polarogram and plotted in Figs. 1 and 3.

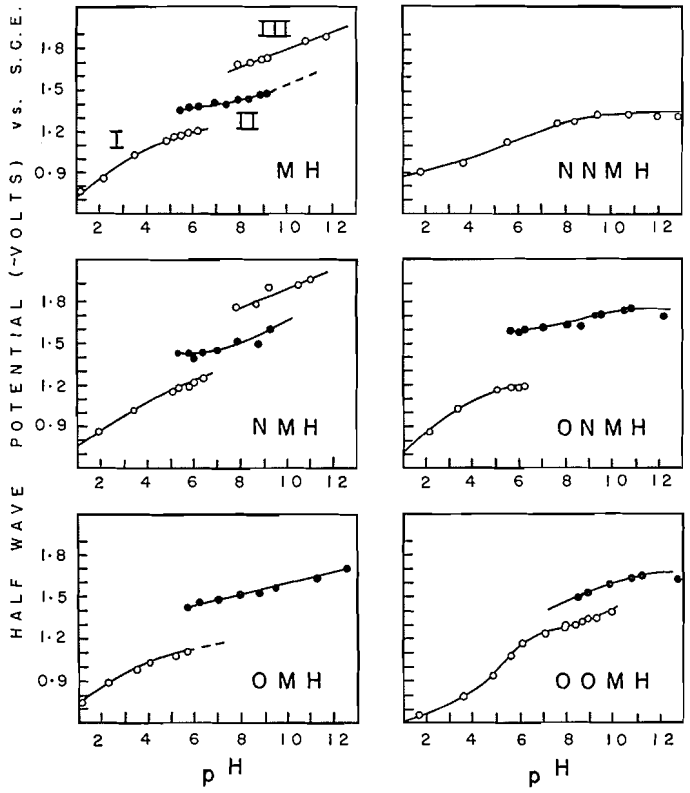


FIG. 3. Polarographic constants as a function of pH for MH and its methyl derivatives.

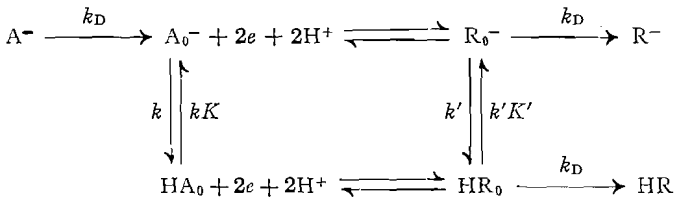
Succinic hydrazide (SH) (tetrahydro-3,6-pyridazinedione) was prepared by the hydrogenation of MH following the procedure of Feuer, Bachman, and White (2). A pK_a of 8.10 was found for this compound using a titration method. Polarographically, however, it was found to be inactive, producing neither cathodic or anodic waves.

DISCUSSION

The similarity of the polarographic behavior of NMH to MH is in line with the structural and chemical similarities of these compounds (5) and no further discussion of this derivative is required.

The polarograms produced by the other derivatives were found to be less distinct than those of MH, showing a tendency to be drawn out and in many cases merging with the hydrogen discharge wave. For this reason the results obtained are less accurate than those for MH but the over-all form of the curves in Figs. 1 and 3 is probably correct. Double waves are produced by all compounds having a —C=N— group (all derivatives except NNMH), which indicates that the second wave may be due to the reduction of this bond rather than the —C=C— group. Measurement of the relative wave heights as a function of mercury pressure, however, indicates that all these waves are kinetic in nature and thus do not arise in the same way as the second set of double waves of MH. Since no clue to the polarography of MH is furnished by these compounds, no further work was done on them and they must be reported here without theoretical explanation.

One piece of evidence which does lead to a possible explanation for the second set of waves of MH, however, is the pK_a value for SH, which was found to be 8.10. This is identical with the crossover point for these waves as obtained from Fig. 1, a replot of the original data (4). SH would be present then as both anion and undissociated acid at pH's for which the double waves occur. Thus, assuming that it is the product of the reduction of MH, the following reaction mechanism will apply:

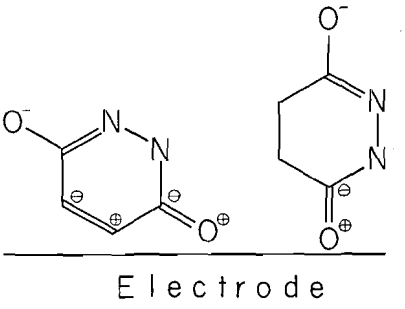


where A^- and HA, and R^- and HR, are the dissociated and undissociated forms of MH and SH respectively in the solution bulk; A_0^-, HA_0, R_0^-, and HR_0 are the same species at the solution–electrode interface; k and k' are the association rate constants for MH and SH, and K and K' their equilibrium constants. The diffusion rate constants of all species are taken as being equal to k_D to simplify calculations.

For the usual kinetic waves the rate of association is considered as of the same order or smaller than the rate of diffusion. However, in the present case

the association reactions are assumed to be very fast relative to diffusion and the electrode reactions virtually instantaneous, leading to an over-all diffusion controlled process. The relative concentrations of the various species is determined by the kinetic balance of the electrode and association reactions, and an analysis of these processes will follow. Firstly, however, we must consider an obvious objection to this mechanism, namely the irreversibility of the over-all reaction as evidenced by the inability of SH to oxidize at the D.M.E.

The orientation of a molecule in the powerful electric field at the solution electrode interface will be determined by the dipoles, either permanent or induced, which it possesses. A double bond, for example, readily forms a dipole which will be attracted toward the electrode, placing it in position to accept electrons. Saturated bonds, since they do not readily form dipoles, tend to assume a position away from the electrode making the exchange of electrons difficult. On this basis then, MH and SH would be oriented thus



Immediately following the reduction of the double bond and before sufficient time for reorientation has elapsed, SH has the same position as MH and may be readily oxidized. Thus, if the electrode and association reactions occur in less time than reorientation a state of instantaneous equilibrium exists and the above mechanism is valid. The assumption that some such energy barrier exists must be implied in the present discussion.

Fig. 4 defines the various currents which will be referred to below. Here

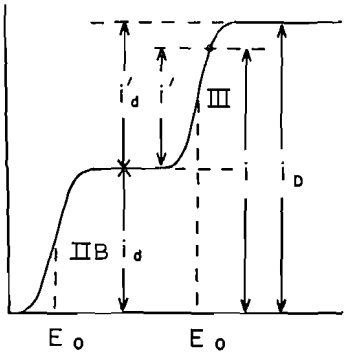


FIG. 4. Definition of currents referred to in the derivation of equation for waves IIB and III.

we see that i_D is the total diffusion current, i_d and i_d' are the individual diffusion currents of waves IIB and III, i is the total current at any point on curve IIB or III, and $i' = (i - i_d)$ the current for wave III alone.

Since the electrode reactions are considered to be rapid and reversible the Nernst equation will give the ratios of the two oxidized and reduced pairs, thus

[1] $$[HA_0]/[HR_0] = (1/[H^+]^2) \exp[2F(E-E_0)/RT] = \epsilon$$

and

[2] $$[A_0^-]/[R_0^-] = (1/[H^+]^2) \exp[2F(E-E_0')/RT] = \epsilon'$$

where F is the Faraday, R the gas constant, T the absolute temperature, E the applied voltage, and E_0 and E_0' the standard potentials of the two systems.

A steady state is rapidly established for any applied voltage so we may write

[3] $$d[HR_0]/dt = k[H^+][A_0^-] - kK[HA_0] + k'[H^+][R_0^-] - k'K'[R_0] = 0.$$

MH is almost completely ionized in the pH range under consideration so that the only form diffusing to the electrode is A^-, and by following the usual polarographic procedure we find

[4] $$[A_0^-] = (i_D - i)/k_D.$$

This combined with [2] leads to

[5] $$[R_0^-] = (i_D - i)/\epsilon' k_D,$$

and since $i = k_D ([HR_0] + [R_0^-])$, then

[6] $$[HR_0] = i/k_D - (i_D - i)/\epsilon' k_D,$$

[7] $$[HA_0] = \epsilon[i/k_D - (i_D - i)/\epsilon' k_D].$$

Substitution of expressions [4], [5], [6], and [7] into [3] and rearranging results in the equation for the two waves:

[8] $$\frac{i}{i_D - i} = \frac{[H^+] + \alpha K}{\beta + K\epsilon} + \frac{\beta}{\beta + K\epsilon}\left(\frac{[H^+] + K'}{K'}\right)\frac{1}{\epsilon'}.$$

where $\beta = k'K'/k$ and $\alpha = \epsilon/\epsilon' = \exp[2F(E_0' - E_0)/RT]$.

From equation [8] we can see that when the applied voltage is large compared with E_0 and E_0' both ϵ and ϵ' will be large and i will be virtually zero. As the applied voltage decreases and approaches E_0, ϵ' will still be large while ϵ will be of order one and expression [8] reduces to

[9] $$(i_D - i)/i = (\beta + K\epsilon)/([H^+] + \alpha K).$$

For values of E that are small compared to E_0 but still large compared to E_0', ϵ approaches zero and the current is independent of E assuming the constant value i_d so that [9] may be written

[10] $$(i_D - i_d)/i_d = \beta/([H^+] + \alpha K).$$

For the special case of $i_d = i_D/2$ occurring at the crossover point for which the hydrogen ion concentration is $[H^+]_{\frac{1}{2}}$, $\alpha K = \beta - [H^+]_{\frac{1}{2}}$ which, when introduced into [10], results in an expression for β:

$$[11] \qquad \beta = ([H^+]-[H^+]_{\frac{1}{2}})(i_D-i_d)/(2i_d-i_D).$$

Using the value of 8.1 for the crossover point obtained from Fig. 1, $[H^+]_{\frac{1}{2}}$ becomes 8.0×10^{-9} M./l. and on substitution of data from the original publication (4) into [11] an average value of 1.0×10^{-8} M./l. is obtained for β (see Table I). Since $K = 2.24\times10^{-6}$ M./l. and $K' = 8.0\times10^{-9}$ M./l., using the above value for β we find the ratio of the rate constants $k'/k = 1.26$ and the difference in the standard potentials $E_0-E_0' = 92$ mv.

TABLE I

DETERMINATION OF β FROM DATA GIVEN IN (1)

pH	i_d, μa.	i_D, μa.	β, $\times10^{-8}$M./l.
7.87	1.57	2.63	1.14
8.38	1.02	2.64	1.03
8.88	0.66	2.60	1.01
9.18	0.51	2.51	0.99

The complete equation for wave II obtained from expressions [9] and [10] is

$$E = E_0+0.030\log\left(\frac{i_d-i}{i}\right)-0.030\log\left(\frac{1}{[H^+]^2}\,\frac{K}{[H^+]+\beta+\alpha K}\right)$$

and the half wave potential

$$[12] \qquad E_{\frac{1}{2}} = E_0-0.030\log\left(\frac{1}{[H^+]}\,\frac{K}{[H^+]+1.2\times10^{-8}}\right).$$

Equation [12] predicts that as the hydrogen ion concentration becomes small compared to 1.2×10^{-8} (pH greater than 7.9) the slope of the plot of $E_{\frac{1}{2}}$ against pH should approach a value of 59 mv. per pH unit. The broken line on the MH-II curve of Fig. 3 is of this slope and might well represent an extension of this curve. For pH's less than 7.9 equation [12] predicts that the curve should approach a slope of 89 mv. per pH unit, but it is prevented from doing so in this case by interference from curve I.

Decreasing the applied voltage further causes the appearance of wave III as E approaches E_0'. Since ϵ is by now virtually zero, equation [8] becomes

$$\frac{i}{i_D-i} = \frac{[H^+]+\alpha K}{\beta}+\frac{[H^+]+K'}{K'}\,\frac{1}{\epsilon'};$$

substitution of [10] into this expression leads to the equation for wave III:

$$[13] \qquad E = E_0'+0.030\log\left(\frac{i_d'-i'}{i'}\right)-0.030\log\left(\frac{K'}{\beta[H^+]^2}\,\frac{[H^+]+\beta+\alpha K}{\beta[H^+]+K'}\right)$$

and for the half wave potential

$$[14] \qquad E_{\frac{1}{2}}' = E_0'-0.030\log\left(\frac{0.79}{[H^+]^2}\,\frac{[H^+]+1.2\times10^{-8}}{[H^+]+7.9\times10^{-9}}\right).$$

Since the second fraction in the log term of [14] is approximately unity, the slope of the plot of $E_{\frac{1}{2}}'$ against pH will be 59 mv. per pH unit. A line of this slope has been drawn through the experimental points from (4) to form curve MH-III in Fig. 3 and appears to fit these points reasonably well.

The proposed mechanism gives at least a qualitative explanation of the second set of double waves of MH. If this is assumed to be correct, wave IIB might more accurately be described as an 'equilibrium' wave rather than a kinetic wave, since its height is the result of an equilibrium between reduction by one path (via the undissociated acid) and oxidation by another (via the anion). To the author's knowledge, maleic hydrazide is a unique example of this type of mechanism, but other examples no doubt will be found.

ACKNOWLEDGMENTS

The author is indebted to Mr. R. W. White of this laboratory for the synthesis of succinic hydrazide and the methyl derivatives of maleic hydrazide used in this work, and to Mr. B. L. Huston for technical assistance.

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THE SYNTHESIS OF THE UROPORPHYRINS II AND IV[1]

By S. F. MacDonald and K. H. Michl[2]

ABSTRACT

Uroporphyrin II and uroporphyrin IV have been synthesized by rational methods. The former has also been separated from a mixture of uroporphyrins previously synthesized.

Hans Fischer's structure for uroporphyrin I was confirmed by the completion of the analytical proof and by synthesis (22*a*). The structure of the remaining three isomers of type II, III, and IV followed by definition, and the porphin-tetraacetic acid-tetrapropionic acid mixture previously synthesized (19*b*) was thus shown to be a mixture of uroporphyrins.

The uroporphyrins frequently occur naturally as inseparable mixtures of isomers and there appear to be no reliable natural sources of the pure types except of uroporphyrin I, which is obtained from urine in cases of congenital porphyria (3). In some cases, but not all, the uroporphyrin from the urine of patients with acute porphyria (23, 24*c*, 26) and from turacin (9, 24*b*, 25, 28) is apparently uroporphyrin III. The assumption that only the uroporphyrins I and III can occur naturally is hardly justified; porphobilinogen, which can give rise to presumably complex mixtures of uroporphyrins (27), is now known to occur widely. The synthesis of the hitherto unknown uroporphyrins II and IV was required to make all four isomers in some degree available for the development of adequate methods of separating and identifying them.

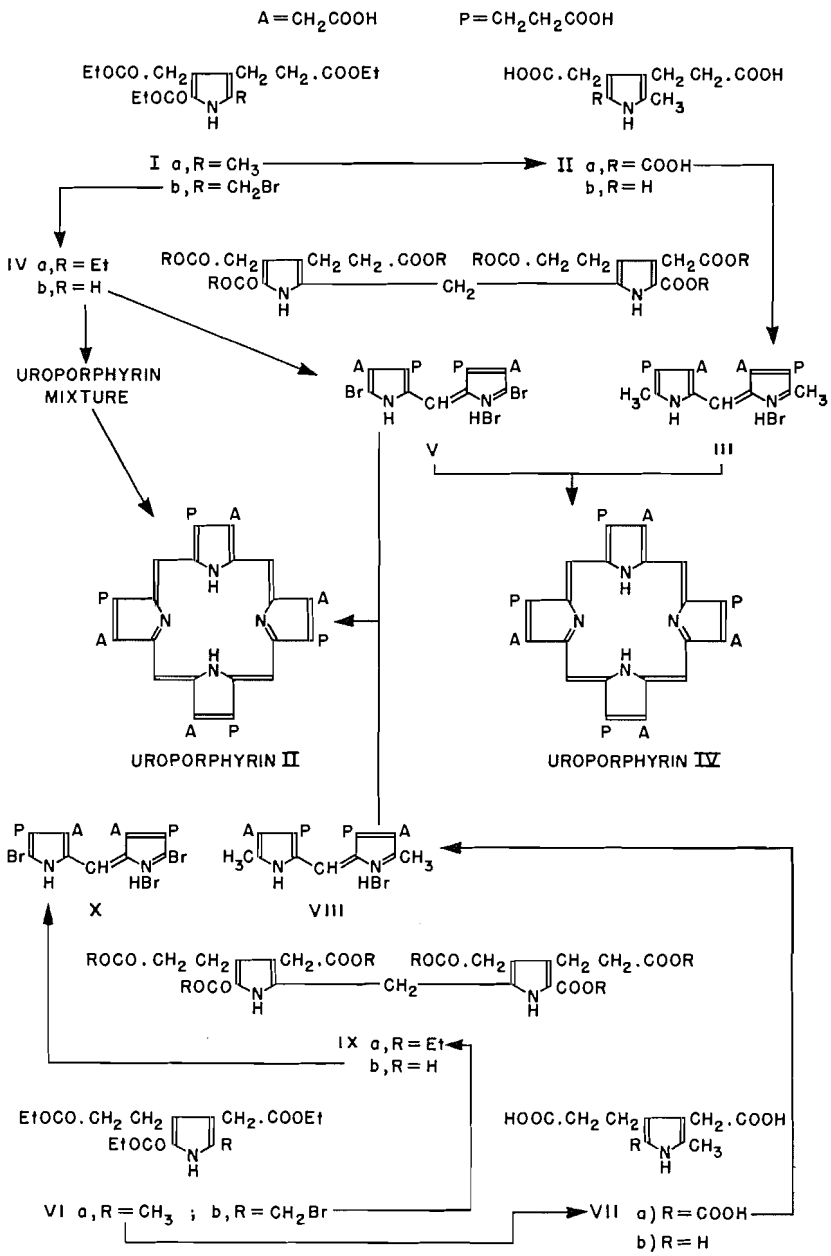
Chart 1 shows how I*a* and VI*a* were converted into the four symmetrical pyrromethenes III, V, VIII, and X. Any three of these should lead to both uroporphyrin II (from III and X or from V and VIII) and uroporphyrin IV (from III and V or from VIII and X). We had already obtained III and VIII from II*a* and VII*a* respectively with formic acid and hydrobromic acid (22*b*).

The bromination of I*a* in carbon disulphide had given crude I*b* as an unanalyzed oil (19*b*). This oil crystallizes on repeated evaporation of its solutions in ether, presumably as a hydrobromide of I*b*, for on recrystallization from warm solvents hydrogen bromide is lost and the more soluble and lower melting I*b* separates. The crude oily I*b* had been converted into IV*a* by boiling with water and thence into IV*b* by hydrolysis (19*b*); better yields are obtained from the "hydrobromide". The pyrromethene V resulted when IV*b* was brominated in formic acid.

By the same procedure VI*a* (22*b*) was brominated to VI*b*, an initially oily product and a crystalline "hydrobromide" being again encountered as intermediates. When it was boiled with water, the "hydrobromide" gave IX*a*, which was hydrolyzed to IX*b*. Being very insoluble in inert solvents, the latter

[1]*Manuscript received August 29, 1956.*
Contribution from the Division of Pure Chemistry, National Research Council, Ottawa. Issued as N.R.C. No. 4138. This work was reported in part at the Ciba Symposium on Porphyrin Biosyntheses and Metabolism, 1955 (21a).
[2]*National Research Council Postdoctorate Fellow, 1953–1954.*

CHART I



could not be recrystallized or brominated by the usual methods and analyzed poorly. However, X was obtained from IX*b* by using a very large excess of a strong solution of bromine in formic acid, a technique which Dr. E. J. Tarlton had developed for brominating the unsymmetrical isomer of IV*b* and IX*b* (unpublished).

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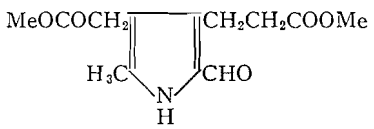
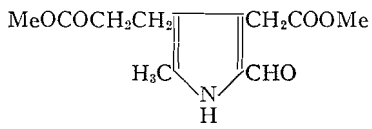
The uroporphyrins II (5%) and IV (3%) resulted when V was heated in methylsuccinic acid at 135° with VIII and III respectively, the melts being worked up by esterifying and partitioning between chloroform and aqueous resorcinol (cf. 22*a*). These syntheses are analogous to those of the coproporphyrins II and IV carried out at higher temperatures (4*b*, 12). Although uroporphyrin I had been obtained in 6% yield at 118° (22*a*), the yield of uroporphyrin IV at that temperature was only 0.1%.

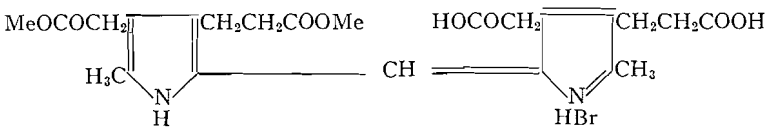
The relationship between the generalities of Fischer's pyrrole and porphyrin syntheses has been discussed (19*a*). Here, as both I*a* and VI*a* were obtained unambiguously by general methods, the necessary pyrromethenes could be prepared using only those of Fischer's methods which were general and unambiguous. Neither his syntheses of coproporphyrin II nor those of coproporphyrin III fulfilled this condition, but the above synthesis of uroporphyrin II represents a general method for type II porphyrins. In the case of type III porphyrins, his synthetic routes also involved the preparation of unsymmetrical pyrromethenes by a method which is not always reliable (1, 10, 17*a*). Thus we found that a synthesis of uroporphyrin III analogous to that of coproporphyrin III (8, 14) broke down when the condensation of XI and II*b* gave the symmetrical III rather than XIII; the alternative condensation of XII (21*b*) and VII*b* gave only unidentified products.



XI



XII



XIII

Unlike other methods of porphyrin synthesis, those from pyrromethenes give essentially pure isomers but require temperatures which might decarboxylate the acetic acid side chains of the uroporphyrins. Three methods have been described which should preclude this decarboxylation. Two are applicable only to type I and II porphyrins respectively, and are further restricted because the pyrromethenes could only be prepared in special cases: coproporphyrin I was synthesized under alkaline conditions (5) and coproporphyrin II was obtained from a 5,5′-free pyrromethene at 125° (13). By the third method 5-bromo-5′-methyl-pyrromethenes were heated at temperatures sufficiently low to avoid decarboxylation; its success depended on whether or not the yield was then acceptable. Only type I porphyrins had thus been obtained at moderate temperatures (15, 18, 22*a*); although the same method should be applicable to type II porphyrins, the pyrromethenes would not be

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so directly accessible. The syntheses of the uroporphyrins II and IV extend the scope of this method in showing that 5,5′-dibromo-pyrromethenes may be combined with 5, 5′-dimethyl-pyrromethenes at moderate temperatures, a combination which would also be necessary for the synthesis of uroporphyrin III.

Turning to the uroporphyrin mixture previously synthesized (19*b*) this offered opportunities of developing methods for the separation of the pure isomers and might prove a useful source of these in view of the low yields associated with rational syntheses. It was more uniform than naturally occurring mixtures and, particularly as now obtained in 40% yield from I*a*, more easily available. The mixture had been synthesized by a method which generally gives some type II porphyrin as the rational product and by analogy to coproporphyrin II, uroporphyrin II was expected to form the least soluble and highest melting of the uroporphyrin methyl esters. However, to the extent that the synthesis was irrational and completely random, uroporphyrin III and to a lesser degree uroporphyrin IV would be favored.

Uroporphyrin II was demonstrated in the uroporphyrin mixture by partially decarboxylating the mixture to coproporphyrins (17*b*), which, as methyl esters, were alternately partially extracted with boiling ether and crystallized from chloroform–methanol until the melting point of 275–283° clearly indicated coproporphyrin II. The yield of coproporphyrin II was much below 10%, the probable limit of sensitivity of the tests for heptacarboxylic and lower acids in the uroporphyrin mixture, and conceivably the coproporphyrin II could have arisen entirely from these rather than from uroporphyrin II. This possibility is excluded by making either of two reasonable assumptions about the conditions under which the uroporphyrin mixture was synthesized: that they precluded decarboxylation or that they precluded type-specific decarboxylation. In a natural uroporphyrin mixture where there is no a priori basis for such assumptions, the above evidence would be inconclusive unless the yield of the coproporphyrin isomer were higher.

Some fractionation of coproporphyrin mixtures is usually easily achieved by conventional methods of crystallizing porphyrins. However, only porphyrins of questionable purity had been isolated from gross mixtures of isomers. The coproporphyrin I, II, III, and IV methyl esters were thus obtained melting at 245° (8), 276° (4*a*), 135° (8), and 177° (7) instead of at 252°, 286°, 145°, and 183° respectively.The type II tetramethyl-porphin-tetrasuccinic acid methyl ester similarly isolated (10), although having the correct melting point (16) is not thus distinguished from a mixture which degraded to a very low melting coproporphyrin II methyl ester (11).

The conventional methods for crystallizing porphyrins either as esters or as free acids did not usefully change the ester melting point of the uroporphyrin mixture and only homogeneous crystalline phases resulted. However, uroporphyrin II was first obtained from it. As shown in Table I, crystallization of the methyl esters from pyridine raised the melting point 35°, giving a product which could be effectively recrystallized first as the methyl ester then as the more soluble and lower-melting ethyl ester. The fractionation was followed by

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TABLE I

SEPARATION OF UROPORPHYRIN II FROM THE UROPORPHYRIN MIXTURE

		Loss, mgm.
Methyl ester, 10 gm., m.p. 256–258°		
(→copro. m.p. 135° and 180° (19*b*))		
From 300 ml. pyridine	→935 mgm., m.p. 285–302°	9065
From 40 ml. chloroform and 400 ml. acetone	→453 mgm.	482
" " " " " "	→394 mgm., m.p. 308–313°	59
" " " " " "	→368 mgm., m.p. 305–310°	26
" " " " " "	→339 mgm., m.p. 305–310°	29
" " " " " "	→326 mgm., m.p. 314–317°	13
" " " " " "	→313 mgm., m.p. 309–313°	13
From 40 ml. pyridine	→298 mgm.	15
" " "	→287 mgm., m.p. 310–314° (→copro. m.p. 279–283°)	11
Methyl ester, 205 mgm.	→*ethyl* ester, 200 mgm., m.p. 240°, 248°, 248°.	
From 50 ml. acetone	→200 mgm., m.p. 235°, — , 250–251° needles	0
" " "	→189 mgm., m.p. 235°, — , 250–251° needles	11
From 100 ml. acetone	→179 mgm., m.p. — , 250°, 252–253° needles	10
" " "	→165 mgm., m.p. 248°, 251°, 252–253° needles and hairs	14
" " "	→145 mgm., m.p. 247°, 251°, 254–256° hairs	20
" " "	→136 mgm., m.p. 247°, 251°, 252–255° hairs (→copro. m.p. 286–287°)	9

melting point, crystal form, solubility, and by the melting point of the derived coproporphyrin methyl ester. The melting points of the uroporphyrin methyl esters were more or less obscured by charring and those of the ethyl esters were complicated by polymorphism.

Alkoxy and C-methyl (22*a*) determinations as well as paper chromatography of the free acids (24*a*) indicated that these synthetic uroporphyrins were free of heptacarboxylic and lower acids, and paper chromatography showed only tetracarboxylic acid in the derived coproporphyrins. A further examination of all these porphyrins by various paper chromatographic methods has been reported (2).

The uroporphyrin II rationally synthesized was identical with that obtained from the mixture by the following criteria: melting points and mixed melting points of the methyl and of the ethyl esters, the quantitative visible spectra of the methyl esters in chloroform, their infrared spectra, their X-ray powder photographs, and by similar comparisons of the derived coproporphyrins.

The type purity of the synthetic uroporphyrins was confirmed by their partial decarboxylation at 180° to the derived coproporphyrins (17*b*) and their comparison with specimens from Hans Fischer's collection. Unfortunately no pure type II, III, or IV coproporphyrin of known origin remained there as standards of type purity. When both were rationally synthesized, the coproporphyrins rather than the uroporphyrins were considered to be the standards of type purity because the yields of the former are higher and the methods of purification and identification appear more convincing when applied to them.

The uroporphyrin II synthesized by either method gave pure coproporphyrin

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II methyl esters having the expected melting points and mixed melting point (286–289°), and having infrared spectra and X-ray powder photographs identical with those of two somewhat lower melting specimens of Fischer's.

The melting behaviors of the coproporphyrin IV ester from uroporphyrin IV and of one of Fischer's specimens, both of which finally melted at 182–184°, were identical whether alone or mixed. Their X-ray powder photographs were also identical. However, there were some differences in the infrared spectra which were shown to be probably due to polymorphism (see Experimental). Fortunately the forms in these specimens were convertible and their melting behavior showed that polymorphism accounted for the three melting points Fischer reported. Two of Fischer's specimens of melting point 168–169° and 183–184° respectively had previously been related only through their synthesis by the same rational method. The third melting point reported was 177°.

The criteria of purity and the method of separation are less convincing when applied to uroporphyrins and coproporphyrins of type III and IV than when applied to those of type I and particularly II. Further, the more soluble coproporphyrins III and IV are not so easily crystallized without appreciable loss; the possibility of their fractionation makes confirmation of the type purity of the uroporphyrins III and IV through the coproporphyrins less certain.

Some work which will be reported later should be mentioned in this connection. Dr. F. Morsingh has synthesized coproporphyrin III methyl ester by four different rational methods. Two of the products melted at 172–176°, and two at 152–154°, and again at 176–179°. Further, using the pyrromethene III and the unsymmetrical isomer of V and X, Dr. E. J. Tarlton has synthesized a uroporphyrin III which was degraded to a coproporphyrin III methyl ester of melting point 176–179° and otherwise identical with all four of the above higher melting forms. Evidently the methyl esters of the coproporphyrins III and IV are not always distinguishable by their melting points alone, but are distinguishable by mixed melting points or other methods.

Table II summarizes the methods of synthesizing uroporphyrin mixtures which were explored. The infrared spectra differed chiefly in the development

TABLE II

SYNTHETIC MIXTURES OF UROPORPHYRIN METHYL ESTERS

Substrate and method	M.p.	% yield	Max. at 1250 cm.$^{-1}$
IV*b*†	256–258° (19*b*)	55	Strong
IV*b*‡	255–256°	18	Strong
I*b**‡	250–255°	4	Strong
IX*b*†	275–295°	3	Absent
IX*b*‡	260–270°	18	Shoulder
VI*b**‡	252–258°	4	Shoulder
Opsopyrrole-dicarboxylic acid§	252–258° (20)	7	Shoulder
Porphobilinogen‡	253–259°	30	Moderate

**Substrate first hydrolyzed with alkali;* †*with formic acid and air several days at 40°;* ‡*boiled 20 min. with 0.5% HCl, then aerated;* §*boiled 20 min. with 0.5% HCl containing 0.15% formaldehyde, then aerated.*

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of a broad maximum at 1250 cm.$^{-1}$ which is much weaker and narrower in uroporphyrin II and absent in the uroporphyrins I and IV; it may be largely due to uroporphyrin III.

EXPERIMENTAL

The melting point ranges of the porphyrins indicate sintering and complete melting as determined on the Kofler hot-stage with crossed Nichols. The uncorrected melting points of the other compounds were determined in capillaries. The infrared spectra were measured in Nujol mull by Dr. R. N. Jones and Mr. R. Lauzon, the X-ray photographs by Dr. Maria Przybylska, of these laboratories.

We are grateful to Professor A. Treibs for the following coproporphyrins from Hans Fischer's collection. A coproporphyrin II methyl ester of Lamatsch was dissolved in chloroform, filtered through a column of alumina, and crystallized from chloroform–methanol. Then after changes in the solid phase at about 170° and 250°, it sintered at 273° and melted at 278–282°; all the reported coproporphyrin II syntheses by Lamatsch were rational, giving pure products of melting point 286–288° (*4b*, 6, 13). Another sample, "isocoproporphyrin" ethyl ester separated from a mixture by Andersag (m.p. 258° (*4b*)), was found to melt at 251–254°, after a change in the solid phase at 230–240° and sintering from 245°; it was hydrolyzed and converted into a coproporphyrin II methyl ester of melting point 280–281° after solid phase changes at about 170° and 270°. The coproporphyrin IV methyl ester of Hiernis (m.p. 177° (8)), for which we found melting point 179–184°, was recrystallized from methanol. Then the yellow plates changed at 168–170° with sintering to red rods, m.p. 174–176°, enclosing fine yellow needles, m.p. 182–184°. Though its origin was not further specified, it was presumably rationally synthesized (12, 14) for only a few milligrams have been otherwise reported (7). The melting points previously reported are thus obviously due to polymorphism: 168–169° (14), 177° (8), 182–184° (7, 12).

2-Bromomethyl-3-(2-carbethoxyethyl)-4-carbethoxymethyl-5-carbethoxy-pyrrole, Ib (cf. 19b)

Solutions of 0.5 gm. of bromine and of 1.0 gm. of I*a* in carbon disulphide were mixed and allowed to stand for 20 min., protected from moisture, and illuminated by sunlight and an ultraviolet lamp. The solvent was removed *in vacuo*. The residual oil was converted to orange crystals (hydrobromide?) by being repeatedly dissolved in absolute ether which was evaporated each time *in vacuo* at $\leqslant 20°$. After three recrystallizations from hexane the product was obtained as colorless needles, m.p. 65–66°, not indefinitely stable in air. Found: C, 48.96; H, 5.64; N, 3.45; Br, 19.07%. Calc. for $C_{17}H_{24}NO_6Br$: C, 48.81; H, 5.78; N, 3.35; Br, 19.11%.

5,5'-Dicarboxy-pyrromethane-4,4'-diacetic acid,-3,3'-dipropionic acid IVb (cf. 19b)

The crude crystalline I*b* (hydrobromide?) was obtained as above from 10 gm. of I*a*, 4.75 gm. of bromine, and 70 ml. of carbon disulphide, after it was

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evaporated six times with 50 to 100 ml. of absolute ether. This product was washed with water by decantation, then refluxed for two hours with 200 ml. of water. After the mixture was cooled, the water was decanted off and the residue, IV*a*, dissolved in 90 ml. of hot ethanol, 50 ml. of 10% aqueous sodium hydroxide added, the alcohol boiled off, and the solution heated for three hours on the steam bath in an open flask. The residue was dissolved in 60 ml. of water, filtered with charcoal, and the filtrate saturated with sulphur dioxide at 0°. The pyrromethane, 5.6 gm. (77%), m.p. about 147°, was filtered off, washed with water, and dried *in vacuo*.

5,5'-Dibromo-pyrromethene-4,4'diacetic acid-3,3'-dipropionic acid Hydrobromide, V

A suspension of 758 mgm. of 5,5'-dicarboxy-pyrromethane-4,4'-diacetic acid-3,3'-dipropionic acid, IV*b*, in 1.5 ml. of 98% formic acid was cooled in ice water and 800 mgm. of bromine added. The temperature rose about 10° and CO_2 and HBr were evolved. After five minutes the flask was placed in a desiccator over NaOH for one hour. The desiccator was then slowly evacuated to 40 mm. then after a further hour, to 10 mm. After two hours at this pressure, crystallization was induced by scratching and 5 ml. of acetic acid was added. The product was separated and repeatedly washed (centrifuge) with acetic acid (7×5 ml.) until the washings were faintly yellow. After it had been washed three times with absolute ether and dried *in vacuo*, the product (290 mgm., 30%) formed small brick-red crystals which showed a greenish fluorescence in solution. On being heated, it melted with decomposition at *ca.* 160–205°. Found: C, 35.79; H, 3.19; N, 4.54; Br, 37.20%. Calc. for $C_{19}H_{19}N_2O_8Br_3$: C, 35.48; H, 2.98; N, 4.36; Br, 37.28%.

After recrystallization from acetic or formic acid, the appearance of this product was less satisfactory. When the bromination was carried out in acetic acid, a different product resulted.

The Mixture of Uroporphyrin Methyl Esters (cf. 19b)

The pyrromethane IV*b* (7.5 gm.) was slurried with 100 ml. of 98% formic acid and kept at 35–40° for one week while a stream of air was passed through the mixture, more acid being added to keep the volume constant. The resulting solution was poured into three liters of water and aerated for two days. The solid was centrifuged off, dried, esterified, and isolated as described (19*b*), more being obtained by re-esterifying material rejected in the purification. Yield 4 gm. (55%, or 42% from I*a*).

2-Bromomethyl-3-carbethoxymethyl-4-(2-carbethoxyethyl)-5-carbethoxy-pyrrole, VIb

This was prepared from VI*a* (23*b*) like I*b* from I*a* except that the crystalline intermediate (hydrobromide?) from VI*a* was recrystallized thrice from carbon disulphide and once from hexane. It formed colorless needles, m.p. 92–93°, more stable in air than I*b*. Found: C, 48.98; H, 5.65; N, 3.41; Br, 18.95%. Calc. for $C_{17}H_{24}NO_6Br$: C, 48.81; H, 5.78; N, 3.35; Br, 19.11%.

5,5'-Dicarboxy-pyrromethane-3,3'-diacetic acid-4,4'-dipropionic acid Hexaethyl Ester IXa

The crude crystalline VI*b* (hydrobromide ?) from 1 gm. of VI*a* was washed with water, then refluxed three hours with 15 ml. of water. The product was filtered off from the cooled mixture and dissolved in ether. The ether solution was washed with dilute sodium hydroxide and with water. Evaporation left 453 mgm. (57%), and after this had been drained on tile, the Beilstein test was negative, the melting point 145°. For analysis it was crystallized from ethanol (charcoal) and from heptane giving colorless needles, m.p. 146°. Found: C, 59.77; H, 6.85; N, 4.42%. Calc. for $C_{33}H_{46}N_2O_{12}$: C, 59.78; H, 7.00; N, 4.23%.

5,5'-Dicarboxy-pyrromethane-3,3'-diacetic acid-4,4'-dipropionic acid IXb

To 4 gm. of the ester IX*a* in 22 ml. of hot ethanol 23 ml. of 10% sodium hydroxide was added. Ethanol was boiled off on a hot plate and the residue heated on the steam bath in a stream of air for four hours. The residue was dissolved in 100 ml. of water and the product (2.68 gm., 89%) was precipitated with sulphur dioxide, filtered off, washed with water, and dried *in vacuo*. For analysis, it was dissolved in 5% ammonia, the solution evaporated *in vacuo*, and the residue dissolved in water. The product was precipitated with sulphur dioxide, collected, and washed four times with water (centrifuge); a little sulphur dioxide was added to the last wash to reverse the peptization. The faintly pink powder, m.p. about 206° (decomp.), was insoluble in inert solvents. Found: C, 50.33; H, 4.41; N, 6.06%. Calc. for $C_{21}H_{22}N_2O_{12}$: C, 51.01; H, 4.49; N, 5.67%.

5,5'-Dibromo-pyrromethene-3,3'-diacetic acid-4,4'-dipropionic acid Hydrobromide, X

The pyrromethane IX*b* (500 mgm.) in a 25 ml. conical flask was treated with 6 ml. of a solution of bromine in 98% formic acid (4 gm. of bromine diluted to 10 ml. and shaken to solution). After it had been allowed to stand $1\frac{1}{4}$ hours while protected from moisture, the solution was filtered, and kept in a desiccator at 50 mm. and then at 25 mm. overnight. The crystalline product was slurried with acetic acid, filtered, and washed with acetic acid. It formed needles, 434 mgm. (67%), which darkened but did not melt below 240°. For analysis, it was recrystallized from 10 parts of 98% formic acid, the yellow needles being washed with acetic acid and absolute ether. Found: C, 35.36; H, 3.63; N, 4.24; Br, 36.91%. Calc. for $C_{19}H_{19}N_2O_8Br_3$: C, 35.48; H, 2.98; N, 4.36; Br, 37.28%.

III Instead of XIII by the Condensation of XI with IIb

The aldehyde XI (706 mgm.) (21*b*) was dissolved in 1.9 ml. of acetic acid and 575 mgm. of cryptopyrrole-dicarboxylic acid, II*b* (19*b*), added. The latter dissolved easily and some of the former crystallized out. When a few drops of hydrogen bromide in acetic acid were added while the mixture was cooled in water and stirred, these crystals dissolved while red microcrystals of the methene separated. The mixture stood at 0° overnight, then the crystals (425 mgm., 61%, m.p. 142° (decomp.), found: OMe, 0.0%) were filtered off,

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washed with acetic acid and with dry ether, and dried. For analysis, the product was recrystallized from acetic acid and washed with acetic acid then with dry ether (centrifuge). The melting point 198–200° was unchanged in the mixture with 5,5′-dimethyl-pyrromethene-3,3′-diacetic acid-4,4′-dipropionic acid hydrobromide, III, prepared unambiguously (22*b*). Found: C, 49.38; H, 4.86; N, 5.41; Br, 16.04; OMe, 0.0%. Calc. for $C_{21}H_{25}N_2O_8Br$: C, 49.13; H, 4.91; N, 5.46; Br, 15.57; OMe, 0.0%.

Porphin-1,4,5,8-tetraacetic acid-2,3,6,7-tetrapropionic acid Octamethyl Ester (Uroporphyrin II Methyl Ester)

(*a*) *By Rational Synthesis*

5,5′-Dibromo-pyrromethene-4,4′-diacetic acid-3,3′-dipropionic acid hydrobromide, V, (1.5 gm.) and 5,5′-dimethyl-pyrromethene-4,4′-diacetic acid-3,3′-dipropionic acid hydrobromide, VIII, (1.39 gm., recrystallized from formic acid (22*b*)) were ground together with 12 gm. of methylsuccinic acid and dried for eight hours at 5×10^{-5} mm. In three portions and while protected from moisture, the mixture was kept for six hours at 135° in a tube heated by boiling Cellosolve. Each melt was dissolved in about 10 ml. of boiling water, the solutions diluted to about 350 ml. centrifuged after one hour, and each precipitate washed with 2×100 ml. of 1% acetic acid (centrifuge). As in the case of uroporphyrin I (22*a*), the combined dried precipitates were esterified with methanolic hydrogen chloride and brought into chloroform. The solution was washed, dried, passed through grade V alumina, concentrated to about 50 ml., and pyrromethenes removed by extraction with 50% (w/w) aqueous resorcinol (8×10 ml.). The solution was washed, dried, concentrated, and the chloroform displaced by methanol. The product (119 mgm., 5.4%, m.p. 305–307°) separated immediately and was washed with methanol (centrifuge). It was recrystallized by extraction into 10 ml. of chloroform, addition of 135 ml. of boiling acetone, and being allowed to cool slowly overnight, giving 96 mgm., m.p. 310.5–315°, after being washed with acetone. A second recrystallization using 8 ml. of chloroform and 100 ml. of boiling acetone gave 88.4 mgm. of fine red needles, m.p. 312–315.5°. The products recovered from the chloroform–acetone mother liquors melted at 305–307° and 306–309° respectively. Found: C, 61.27; H, 5.58; N, 6.11; OMe, 26.44; C-Me, 0,00%. Calc. for $C_{48}H_{54}N_4O_{16}$: C, 61.14; H, 5.77; N, 5.94; OMe, 26.33; C-Me, 0.00%.

A sample was hydrolyzed and chromatographed on paper with 2,4-lutidine–water showing two spots with the same R_f values as those of uroporphyrin I (24*a*).

(*b*) *From the Uroporphyrin II Ethyl ester* (*b*) *Separated From the Mixture*

The ester (15.2 mgm.) was hydrolyzed on the steam bath with aqueous–alcoholic potassium hydroxide, the alcohol evaporated, and the porphyrin precipitated with acetic acid. It was esterified with methanolic hydrogen chloride, brought into chloroform, and the chloroform solution washed, then filtered, and washed through a column of grade V alumina. The solution was concentrated and the chloroform displaced by methanol. The product (7 mgm.) which separated was recrystallized twice from chloroform–methanol and once

from chloroform–acetone giving 6.7 mgm., m.p. 311–315° (4°/min.) with some charring.

Specimens obtained as under (*a*) and (*b*) showed an unchanged mixed melting point and identical quantitative visible spectra in chloroform, infrared spectra, and X-ray powder photographs.

The C-methyl content of the uroporphyrin methyl ester of Table I after six crystallizations from chloroform–acetone was 0.00%. This ester, although incompletely purified, gave an X-ray powder photograph and an infrared spectrum identical with those of the purest specimens.

Porphin-1,4,5,8-tetraacetic acid-2,3,6,7-tetrapropionic acid Octaethyl Ester (Uroporphyrin II Ethyl Ester)

(*a*) *From the Rationally Synthesized Methyl Ester*

Uroporphyrin II methyl ester (5.2 mgm. of preparation (*a*)) was hydrolyzed in 2 ml. of concentrated hydrochloric acid for 20 hr. at 20°. The solution was then freeze-dried and the residue left for 20 hr. in saturated ethanolic hydrogen chloride. This solution was poured into ice water and extracted with chloroform which was then washed with water, with very dilute sodium hydroxide, and twice with water. After the extract had been dried over sodium sulphate, chloroform was displaced from the boiling solution, with ethanol. As the solution cooled slowly, the product (4.2 mgm.) separated as very thin needles, m.p. 249.5–253°, the cooled melt resolidifying to prisms of melting point 233–245°.

(*b*) *From the Synthetic Uroporphyrin Mixture*

The fractionation of the mixture is summarized in Table I. The porphyrins were dissolved either by being refluxed with pyridine for a few minutes, or extracted into chloroform (thimble) followed by addition of boiling acetone to the hot solution, or extracted into acetone (thimble). The hot solutions were allowed to cool slowly and undisturbed to room temperature in the dark, the first crystallization from pyridine being collected after seven days and all subsequent crystallizations after one day. Crystals from pyridine were recrystallized from chloroform–methanol before determination of the melting point, which was otherwise completely obscured by charring.

The significance of the temperatures given in the table to describe the melting behavior of the uroporphyrin II ethyl esters is illustrated by those applying to the final product: sintering began at 247°, the original crystals were replaced by prisms and a little melt at 251°, and melting of the prisms began at 252° and was complete at 255°. Found: C, 63.95; H, 6.83; N, 5.23; OEt, 33.88%. Calc. for $C_{56}H_{70}N_4O_{16}$: C, 63.74; H, 6.69; N, 5.31; OEt, 34.16%.

The mixed melting point with preparation obtained as under (*a*) showed no depression.

1,4,5,8-Tetramethyl-porphin-2,3,6,7-tetrapropionic acid Tetramethyl Ester (Coproporphyrin II Methyl Ester) from Uroporphyrin II

(*a*) *From rationally Synthesized Uroporphyrin II Methyl Ester*

Uroporphyrin II methyl ester (6 mgm., the preparation (*a*) rationally synthesized) was heated for four hours in a sealed tube at 185–190° with

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4.5 ml. of 1% hydrochloric acid. The solution was separated from needles of the coproporphyrin hydrochloride, which were dissolved in concentrated hydrochloric acid. To precipitate the porphyrin the combined filtrates were saturated with salt and disodium hydrogen phosphate was added. The precipitate was separated, washed with very dilute acetic acid, and esterified with methanolic hydrogen chloride. The ester was brought into chloroform after addition of ice and water, and the chloroform was washed with water, very dilute sodium hydroxide, and water, dried over sodium sulphate, filtered, and displaced by methanol at the boil. The product (3.0 mgm.) separated as long rods, m.p. 286–289°. Found: C, 67.27; H, 6.49%. Calc. for $C_{40}H_{46}O_8N_4$: C, 67.59; H, 6.52%.

After hydrolysis, paper chromatography with 2,4-lutidine–water revealed a single spot with the same R_f value as that observed when the coproporphyrin IV methyl ester of Hiernis was similarly treated.

(*b*) *From Uroporphyrin II Ethyl Ester Separated from the Mixture*

Uroporphyrin II ethyl ester (9.9 mgm., preparation (*b*)) in 10 ml. of 1% hydrochloric acid was held under vacuum at 0°, then heated for four hours at 190° in a sealed tube. The needles were dissolved by adding ammonia, and the porphyrin was precipitated with acetic acid after the solution had been filtered and heated. The product was obtained as under (*a*) above except that the chloroform solution was filtered through a column of grade V alumina. It formed prismatic needles (4.6 mgm.), m.p. 285–289° after apparent changes in the solid phase at about 170° and at 270°. After recrystallization by extraction with boiling chloroform (thimble) and displacement of the chloroform with methanol, 4.6 mgm. (62%) was obtained and the mother liquor was colorless. It then formed long prismatic needles, m.p. 286–287° (1°/min.), again showing apparent solid phase changes at about 170° and 270°.

Its melting point was not depressed when mixed with the ester obtained as under (*a*) and the visible spectra of the two in chloroform were identical. The infrared spectra and X-ray powder photographs of these two and of the reference specimens (Andersag and Lamatsch) were identical, and the ester (*b*) did not depress the melting point of Andersag's specimen.

The X-ray powder photographs of a coproporphyrin II methyl ester from a partially purified uroporphyrin II ethyl ester indicated that a second form existed which was only partially converted into the usual one by heating.

Porphin-1,4,6,7-tetraacetic acid-2,3,5,8-tetrapropionic acid Octamethyl Ester (Uroporphyrin IV Methyl Ester)

(*a*) At 117°: Using 500 mgm. of 5,5′-dibromo-pyrromethene-4,4′-diacetic acid-3,3′-dipropionic acid hydrobromide, V, 500 mgm. of 5,5′-dimethyl-pyrromethene-3,3′-diacetic acid-4,4′-dipropionic acid hydrobromide, III, and 4 gm. of methylsuccinic acid, the method was that used in the analogous synthesis of uroporphyrin II, except that it was fused in one lot at 117°, the tube being heated with boiling acetic acid. Worked up in the same way, the more soluble uroporphyrin IV ester (0.9 mgm., 0.12%), m.p. 254–258.5°, separated when the methanol solution was cooled slowly. After recrystallization from 5 ml. of methanol, 0.6 mgm. was obtained, m.p. 256–259°.

(*b*) At 135°: As in the analogous synthesis of uroporphyrin II, 2 gm. of V, 2 gm. of III, and 16 gm. of methyl succinic acid were heated at 135° in four lots and the ester isolated. After washing of the ester with methanol until the washings were nearly colorless, 47 mgm. was obtained, m.p. 250–256°. Here the aqueous and methanolic mother liquors and washings showed a strong porphyrin spectrum. They were therefore combined and centrifuged. The precipitate was esterified and worked up as above giving an additional 49 mgm. of uroporphyrin IV ester, m.p. 250–255°, total yield 3.3%. After two recrystallizations from acetone (thimble), 77 mgm. was obtained, m.p. 255.5–259.5°. Found: C, 61.28; H, 5.64; N, 6.10; OMe, 26.61; C-Me, 0.00%. Calc. for $C_{48}H_{54}N_4O_{16}$: C, 61.14; H, 5.77; N, 5.94; OMe, 26.33; C-Me, 0.00%.

Both the esters (*a*) and (*b*) were amorphous but crystallized at 245° before melting. Their mixed melting point was undepressed and their quantitative visible spectra in chloroform were identical. Determined on samples which had been crystallized at 245°, their X-ray powder photographs were identical. Their infrared spectra had broad bands and diffuse structures, differing only in two shoulders and a maximum which were peculiar to the presumably less pure (*a*) and large enough to be distinct.

After hydrolysis, both specimens showed only two spots with the same R_f's as the reference uroporphyrin I (24*a*).

1,4,6,7-Tetramethyl-porphin-2,3,5,8-tetrapropionic acid Tetramethyl Ester (Coproporphyrin IV Methyl Ester) from Uroporphyrin IV

Uroporphyrin IV methyl ester (10 mgm., preparation (*b*) at 135°) was heated for four hours in a sealed tube at 185–190° with 1% hydrochloric acid. The porphyrin was precipitated from the filtered solution by saturating the solution with salt, adding disodium hydrogen phosphate, and heating. It was esterified and isolated as usual, care being taken to completely replace the chloroform by methanol. The crude material (4.7 mgm., 63%) had melting point 165–168°, some small yellow needles melting at 181–183°. After recrystallization from 5 ml. of methanol the product (3.8 mgm.) formed yellowish plates, sintering and changing to red rods enclosing yellow needles at 168–170°; the red rods melted at 174–176°, the yellow needles at 182–184°. Found: C, 67.34; H, 6.30%. Calc. for $C_{40}H_{46}N_4O_8$: C, 67.59; H, 6.52%.

After hydrolysis, paper chromatography with 2,4-lutidine–water showed only a coproporphyrin spot (24*a*).

The melting behavior of this ester was identical with that of Hiernis's specimen, separately or mixed. Their quantitative visible spectra in chloroform and their X-ray powder photographs were identical. Their infrared spectra had broad bands and diffuse structures; the specimen from uroporphyrin IV differed in lacking a small shoulder at 1260 $cm.^{-1}$, and in lacking a small minimum and two small maxima in the 900–1100 $cm.^{-1}$ region where its general absorption was the higher of the two. Recently the infrared spectrum of a high-melting form of coproporphyrin IV ester, synthesized here according to Fischer (14), showed that these differences were consistent with the specimen from uroporphyrin IV being a mixture of the two forms. It is probable that

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mulling partially converted that from uroporphyrin IV to the higher-melting form, as we have shown with one sample of synthetic coproporphyrin III ester whose X-ray powder photograph and infrared spectrum presented the same anomaly.

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THE INFRARED SPECTRA OF SECONDARY AMINES AND THEIR SALTS[1]

By R. A. Heacock[2] and Léo Marion

ABSTRACT

The infrared spectra of a number of secondary bases and of their salts have been examined. The spectra of the salts differ from those of the corresponding bases in containing several absorption bands that are absent from the latter. Those of the new bands occurring in the region 1620 to 1560 cm.$^{-1}$, which are due to NH_2^+ deformation vibrations, are characteristic of secondary amine salts, and can be used to detect the presence of a secondary amino group in the original molecule. With aromatic bases the spectra are complicated because the ring absorption occurs in the same region, but in many cases the assignment can still be made, although with less certainty. In zwitterionic substances such as the secondary aliphatic amino acids, the function is more difficult to detect.

The secondary amino group is found in many naturally occurring substances, but it has proved sometimes tedious and costly in material to identify it chemically. It was observed that the infrared absorption spectrum of *pseudo*-conhydrine hydrochloride presented a number of marked differences in absorption from that of the free base, particularly in the region around 1600 cm.$^{-1}$. If these differences could be shown to be characteristic of the secondary amino group in its protonated form, a physical method of identifying this function would become available, which would be extremely useful in the investigation of compounds of unknown constitution. An investigation has thus been made of the infrared spectra of a number of secondary amines and their simple salts.

The primary amino group gives rise to two NH stretching bands in the region 3500–3300 cm.$^{-1}$, and another band between 1650 and 1560 cm.$^{-1}$ due to the NH deformation vibrations (3, 16). It also absorbs in the long wavelength region of the spectrum, and these bands have been alternatively described as NH twisting (16) or rocking vibrations (6). The secondary amino group shows only one band in the NH stretching region while the deformation vibrations of the group are usually too weak to be of use for identification purposes (3), and occur at frequencies lower than those of the primary amino group. This has recently been substantiated by Barr and Haszeldine (2).

Salt formation has been shown to modify the NH stretching absorption in amines. There are, however, differences in frequency between the NH stretching vibrations associated with the $-NH_3^+$, $>NH_2^+$, and $>NH^+$ groupings. In an investigation of the infrared spectra of aliphatic primary amines and their salts, Depas and Khaladji (8) observed that the free bases have a sharp strong band at *ca.* 3226 cm.$^{-1}$ due to NH stretching and that this band is greatly reduced in intensity in the spectra of the hydrochlorides. They also observed new bands, possibly associated with NH stretching,

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appearing between 2565 and 2400 cm.$^{-1}$ and near 2000 cm.$^{-1}$ in the spectra of the salts. The spectrum of butylamine shows a band at 3333 cm.$^{-1}$, and that of its hydrochloride contains bands in the regions 3180–3030 cm.$^{-1}$, 2625–2590 cm.$^{-1}$, and near 2525 cm.$^{-1}$ (10).

The spectra of primary aliphatic amino acids, which are zwitterionic in the solid state, show the $-NH_3^+$ stretching absorption between 3180 and 3030 cm.$^{-1}$ and between 2630 and 2500 cm.$^{-1}$ (10). In the spectra of the amino acid hydrochlorides, the position of this band is not quite so clear since the salts do not all absorb in this region. According to Randall *et al.* (16) the hydrochlorides of amino acids show a series of moderate intensity bands between 3030 and 2500 cm.$^{-1}$, and also in the region 2140 to 2080 cm.$^{-1}$. A band at 2100 cm.$^{-1}$ has also been observed in the spectra of simple amino acids (20). Lenormant (13) has shown that the band structure observed between 3175 and 2630 cm.$^{-1}$ assigned to the $-NH_3^+$ group in the spectrum of glycine moves, on deuteration, to 2210–1955 cm.$^{-1}$ (with the exception of the CH stretching bands), thus confirming the assignment. The corresponding absorptions for secondary and tertiary amino acids have not so far been clearly defined (3).

Recently "ammonium" and "immonium" bands have been defined (22, 23, 27); the former, indicative of the group $\diagup\!\!\diagdown\overset{+}{N}\diagup\!\!\diagdown_{H}$, is observed as an intense band between 2440 and 2350 cm.$^{-1}$; the latter is supposedly due to the $=\overset{+}{N}\diagup_{H}$ group and is manifested as a number of sharp bands of a somewhat lower intensity between 2100 and 1980 cm.$^{-1}$.

Stretching vibrations of the NH^+ group are considerably displaced towards lower frequencies. Lord and Merrifield (14) have observed that in the spectrum of triethylamine hydrochloride the NH^+ stretching band occurs at 2540 cm.$^{-1}$, while in that of pyridine hydrochloride a broad structureless band is found at 2450 cm.$^{-1}$ and a doublet with peaks at 2090 and 1980 cm.$^{-1}$.

Amines are known to give rise to absorption in the region of the spectrum associated with hydrogen bending vibrations, and these bands have been assigned to $-NH_2$ and $\diagup\!\!\diagdown NH$ deformation vibrations. As yet, however, there is not complete agreement about the assignment of NH deformation vibrations (19), except for simple primary amines in which case the absorption occurs between 1650 and 1590 cm.$^{-1}$. The primary amines studied by Depas and Khaladji (8) had a band of medium intensity at 1613 cm.$^{-1}$ which was unchanged by salt formation. In a study of the infrared spectrum of methylamine vapor, Cleaves and Plyler (5) correlated the spectral bands at 1625 cm.$^{-1}$ and 1516 cm.$^{-1}$ with NH deformation vibrations. Butylamine absorbs at 1613 cm.$^{-1}$ and its hydrochloride at 1603 cm.$^{-1}$ (10). *Iso*hexylamine produces a band at 1613 cm.$^{-1}$ while its hydrochloride shows the corresponding absorption at 1587 cm.$^{-1}$ (9). The spectrum of hydrazine shows the NH_2 deformation band at 1613 cm.$^{-1}$ (18) and that of *N*-methylhydrazine shows the corresponding band at 1587 cm.$^{-1}$ (1).

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The appearance of two bands in 1600 to 1500 cm.$^{-1}$ region, in addition to any ionic carboxyl absorption, appears to be indicative of an amino acid or its hydrochloride which can possess the $-NH_3^+$ group. One or both of these bands may be associated with NH_3^+ deformation vibrations (3, 11, 12, 13, 16). The infrared absorption spectra of *N*-substituted amino acids, in this region, differ from those containing a primary amino group (12) and correlations are difficult owing to the small amount of data available and the complexity of the spectra. However, *dl*-proline absorbs at 1653 cm.$^{-1}$ (11, 12) and sarcosine (16) at 1645 cm.$^{-1}$.

The position of NH deformation bands in aromatic amines is complicated by the fact that this vibration occurs in the same region as the aromatic ring vibrations, and often causes modification of these. Rasmussen and Brattain (17) state that there is often an intensification of the ring vibrations in the spectra of aromatic amines, and this has led several authors to attempt to define characteristic bands of the "anilino" structure. Witkop and Patrick (24) correlate a band at 1613 cm.$^{-1}$ with the grouping $C_6H_5-\underset{|}{N}-C<$, and they further state that a band in the region 1639 to 1600 cm.$^{-1}$ is "characteristic of anilino structures in general and of indolines in particular" (21, 25, 26). On the other hand, according to Randall *et al.* (16) the absorption due to the anilino structure $C_6H_5-N<$ occurs at 1610 to 1595 cm.$^{-1}$, 1590 to 1560 cm.$^{-1}$, and 1515 to 1490 cm.$^{-1}$. Secondary aromatic amines show an intensification of the aromatic band at 1600 cm.$^{-1}$ and possibly a shift of the 1500 cm.$^{-1}$ aromatic bands towards higher frequencies (3).

There is cited in the literature only a relatively small number of cases of bands assigned to deformation vibrations of protonated secondary amino groups. For the hydrochlorides of four dihydroindole derivatives, Witkop, Patrick, and Kissman (27) quote absorptions between 1592 and 1570 cm.$^{-1}$, while Randall *et al.* (16) refer to $-NH_2^+$ deformations of *dl*-proline hydrochloride at 1592 cm.$^{-1}$, and of 2,2-dimethylthiazolidine-4-carboxylic acid hydrochloride at 1553 cm.$^{-1}$.

EXPERIMENTAL

The spectra were recorded on a Perkin–Elmer double beam spectrometer (Model 21) with a sodium chloride prism. The conditions under which the spectra were measured are stated for each substance.

For the purposes of this investigation the following new compounds were prepared.

5,6-Dihydrophenanthridine Hydrochloride

This salt was prepared by the action of dry hydrogen chloride on a solution of the base in dry benzene. It was recrystallized from aqueous alcoholic hydrochloric acid from which it separated as colorless needles, m.p. 198°. Found: C, 71.99; H, 5.13; Cl, 16.33. $C_{13}H_{12}NCl$ requires: C, 71.72; H, 5.56; Cl, 16.29%.

Piperazine Perchlorate

The hydrate of this salt (cf. Data and Chatterjee (7)) was dried at 100° *in vacuo*. The anhydro salt melted at 308° (decomp.). Found: C, 16.87; H, 3.98. $C_4H_{12}O_8N_2Cl_2$ requires: C, 16.73; H, 4.22%.

N-Deuteropiperidinium Deuterochloride

Piperidine hydrochloride (1.0 gm.) was dissolved in heavy water (*ca.* 90% D_2O, 30 ml.) and the solution heated to 80°. After the solution had been cooled, it was evaporated *in vacuo* and the residual partly deuterated salt was caused to exchange twice more with further quantities of heavy water (*ca.* 99.8% D_2O, 10 ml.). The deuterated salt was a white solid, m.p. 247°.

N-Deuteropiperidine

A solution of sodium deuteroxide in heavy water was prepared by dissolving sodium (2.4 gm.) in heavy water (99.8% D_2O, 15 ml.). To the cooled solution *N*-deuteropiperidinium deuterochloride (6.0 gm.) was added and the solution saturated with sodium sulphate. The resulting suspension was extracted with five successive portions of 50 ml. of dry ether. Distillation of the oil obtained after evaporation of the dried combined extract gave the base as a colorless liquid, b.p. 106 to 108°.

RESULTS

The infrared spectra of a number of secondary amines, both simple and complex, and their salts have been recorded. The principal bands observed in four special regions, i.e., I, 4000 to 3000 cm.$^{-1}$; II, 2800 to 2000 cm.$^{-1}$; III, 1700 to 1500 cm.$^{-1}$; IV, 850 to 600 cm.$^{-1}$ are listed below. The relative intensities of the spectral bands are shown in parenthesis, i.e., (s) strong, (m) medium, (w) weak.

Dimethylamine

Gas: I, 3350 (w), 3170 (w); II, 2800 (s), 2900 (w); IV, 742–715 (s).

Dimethylamine Hydrochloride

Solution in chloroform: I, 3650 (w); II, 2740 (s), 2450 (m); III, 1600 (m).

Solid: I, 3200 (m); II, 2800–2775 (s), 2475 (s), 2375 (w), 2320 (w), 2160 (w); III, 1605 (m).

Piperidine

Liquid: I, 3263 (s); II, 2790 (s), 2730 (s), 2675 (m), 2635 (w); III, 1600–1575 (w); IV, 817 (m), 735 (s).

Piperidine Hydrochloride

Nujol mull: I, 3190 (w); II, 2795 (s), 2735 (s), 2640 (s), 2590 (m), 2535 (s), 2440 (m), 2170 (w), 2050 (w), 2015 (w); III, 1672 (w), 1613 (w), 1597 (s); IV, 862 (w).

Morpholine

Liquid: I, 3303 (m); II, 2760 (m), 2690 (w); IV, 833 (s), 800–790 (s).

Solution in carbon tetrachloride: II, 2745 (w).

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Morpholine Hydrochloride

Nujol mull: II, 2780 (s), 2720 (s), 2620 (m), 2470 (m), 2185 (w); III, 1582 (m); IV, 823 (w).

Piperazine

Solid: I, 3235 (s); II, 2750 (s), 2675 (w), 2640 (w), 2520 (w), 2255 (w); IV, 835 (s).

Solution in chloroform: I, 3335 (w); II, 2740 (w), 2510 (w).

Piperazine Hydrochloride

Hydrated, nujol mull: I, 3545 (m), 3475 (m); II, 2785 (s), 2730 (s), 2615 (m), 2565 (m), 2480 (m), 2390 (m), 2140 (w); III, 1627 (s), 1553 (s).

Anhydrous, nujol mull: I, 3540 (m), 3470 (m); II, 2780 (s), 2725 (s), 2620 (m), 2570 (m), 2540 (m), 2480 (m), 2450 (m), 2385 (m), 2190 (w), 2135 (w); III, 1626 (s), 1597 (m), 1552 (s).

Piperazine Perchlorate

Hydrated, nujol mull: I, 3545 (w), 3330 (w), 3200 (s), 3110 (m); II, 2730 (w), 2700 (w), 2600 (w), 2520 (w), 2430 (w), 2175 (w), 2040 (w); III, 1637 (w), 1597 (s); IV, 862 (w), 605–592 (s).

Anhydrous, nujol mull: I, 3190 (s), 3105 (s), 3030 (m); II, 2520 (w), 2420 (w), 2040 (w); III, 1594 (s); IV, 866 (w), 635 (m).

Pyrrolidine

Liquid: I, 3260 (s); II, 2700 (w), 2640 (w); III, 1675–1645 (w); IV, 845–835 (s).

In carbon tetrachloride: II, 2680 (m), 2560 (m), 2450 (w), 2190 (w).

In carbon disulphide: II, 2670 (w), 2585 (w); IV, 800 (w), 755 (w).

Pyrrolidine Picrate[3]

Nujol mull: I, 3075 (s); II, 2610 (w), 2500 (w); III, 1633 (s), 1613 (s), 1575 (s), 1548 (s), 1530 (s); IV, 837 (w), 793 (m), 745 (m), 710 (m).

l-Proline

Nujol mull: I, 3150 (s); II, 2800 (s), 2620 (s), 2520 (s), 2390 (s); III, 1622 (s), 1585 (s), 1567 (s); IV, 847 (w), 790 (w), 640 (w).

l-Proline Hydrochloride[4]

Nujol mull: II, 2703 (s), 2639 (s), 2525 (s), 2433 (s); III, 1592 (m).

Sarcosine[4]

Nujol mull: I, 3448 (m); II, 2451 (w); III, 1645 (m), 1616 (m).

Sarcosine Hydrochloride[4]

Nujol mull: I, 3610 (w); II, 2793 (s), 2710 (s), 2519 (m), 2381 (m); III, 1621 (w), 1570 (w).

[3]*Because of the hygroscopic nature of the hydrochloride of pyrrolidine the picrate was used. The bands at 1633, 1613, 1548, and 1530 cm.*$^{-1}$ *according to Randall et al. (16) are due to picric acid.*

[4]*Values taken from Randall et al. (16).*

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N-Phenylglycine[4]

Nujol mull: I, 3225 (w); II, 2347 (m), 2165 (m), 2004 (m); III, 1567 (s), 1495 (s).

N-Phenylglycine Hydrochloride[4]

Nujol mull: I, 3584 (w), 3425 (w); II, 2688 (s), 2488 (m), 2500 (m), 2387 (m); III, 1600 (w), 1560 (w), 1490 (m).

Diethanolamine

Liquid: I, 3300 (s); IV, 865–850 (w).

Solution in chloroform: I, 3610 (w), 3450–3360 (w).

Diethanolamine Nitrate

Nujol mull: I, 3380 (s), 3155 (s), 3050 (s); II, 2780 (m), 2390 (w); III, 1590 (m); IV, 820 (m), 807 (m), 716 (w), 710 (w).

Solution in chloroform: I, 3675 (w), 3590 (w); III, 1608 (m).

1,2-Diethylhydrazine

Liquid: I, 3245 (s); II, 2675 (w); IV, 845 (s), 805 (s), 735 (s).

Solution in carbon tetrachloride: I, 3205 (w); II, 2700 (m), 2520 (w); IV, 667 (m).

1,2-Diethylhydrazine Hydrochloride

Solid: I, 3205 (s), 3030 (s); II, 2800–2720 (s), 2540 (s), 2420 (m), 2280 (m), 2180 (w); III, 1597 (m), 1542 (m); IV, 861 (s), 812 (s).

N-Ethylaniline

Liquid: I, 3380 (s), 3215 (w), 3050 (s), 3020 (s); II, 2690 (w), 2580 (w), 2322 (w); III, 1608 (s), 1594 (s), 1508 (s); IV, 745 (s), 688 (s).

N-Ethylaniline Hydrochloride

Nujol mull: I, 3160 (w); II, 2750 (s), 2710 (s), 2660 (s), 2600 (s), 2550 (s), 2490 (s), 2390 (s), 2100 (w), 2018 (w); III, 1607 (m), 1600 (w), 1589 (m), 1495 (s); IV, 803 (w), 756 (s), 750 (s), 688 (s).

Diphenylamine

Solid: I, 3365 (m); III, 1603 (s), 1590 (m), 1565 (w), 1522 (s), 1502 (s); IV, 748 (s), 743 (s), 698 (s), 686 (s).

Diphenylamine Hydrochloride

Nujol mull: II, 2755 (m), 2700 (m), 2660 (s), 2590 (s), 2470 (s), 2430 (s), 2350 (s), 2300 (s), 2050 (w), 1990 (w); III, 1600 (m), 1572 (m), 1568 (m), 1502 (s); IV, 805 (w), 757 (s), 752 (s), 735 (s), 696 (s), 680 (s).

1,2,3,4-Tetrahydroquinoline

Liquid: I, 3380 (m), 3020 (w); III, 1610 (s), 1590 (m), 1508 (s), 1505 (s); IV, 837 (w), 818 (w), 742 (s), 712 (w).

[4]*Values taken from Randall et al. (16).*

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1,2,3,4-Tetrahydroquinoline Hydrochloride

Nujol mull: I, 3050 (w); II, 2775 (m), 2690 (s), 2630 (s), 2590 (s), 2520 (s), 2480 (s), 2460 (s), 2420 (s), 2280 (w), 2190 (w), 2100 (w), 2060 (w), 2035 (w); III, 1612 (w), 1597 (w), 1572 (s), 1510 (m); IV, 845 (w), 812 (w), 758 (s), 751 (s), 725 (w), 698 (w).

5,6-Dihydrophenanthridine

Nujol mull: I, 3350 (s), 3290 (s); III, 1611 (s), 1500 (s); IV, 815 (w), 768 (w), 732–722 (s), 685 (w).

5,6-Dihydrophenanthridine Hydrochloride

Nujol mull: II, 2750 (w), 2700 (w), 2650 (s), 2570 (s), 2540 (s), 2420 (s), 2355 (s), 2300 (m), 2202 (w), 2130 (w), 2050 (w); III, 1613 (w), 1577 (w), 1560 (w), 1512 (w), 1494 (m); IV, 815 (w), 805 (w), 756 (s), 735 (w), 718 (w), 630 (w).

N-Methylanthranilic Acid

Nujol mull: 3370 (m); II, 2735 (m), 2650 (m), 2580 (m), 2500 (w); III, 1662 (s), 1587 (s), 1580 (m), 1565 (w), 1524 (s), 1507 (w); IV, 845 (w), 835 (w), 775 (w), 748 (s), 700 (w), 657 (w).

N-Methylanthranilic Acid Hydrochloride

Nujol mull: I, 3270 (s), 3140 (s); II, 2720 (s), 2660 (s), 2600 (s), 2500 (s), 2395 (s), 2000–1800 (m); III, 1692 (s), 1665 (s), 1617 (m), 1542 (s), 1502 (s); IV, 820 (s), 805 (m), 770 (s), 750 (s), 697 (s), 652 (m).

Methyl N-Methylanthranilate

Liquid: I, 3470 (w), 3365 (m), 3000 (w); III, 1685 (s), 1657 (w), 1611 (s), 1585 (s), 1523 (s); IV, 830 (w), 790 (w), 742 (s), 700 (m), 662 (w).

Methyl N-Methylanthranilate Hydrochloride

Nujol mull: I, 3365 (w), 3060 (m); II, 2680 (m), 2600 (m), 2470 (s), 2325 (s), 2270 (m), 2040 (w); III, 1713 (s), 1695 (s), 1615 (m), 1590 (m), 1542 (m), 1527 (m), 1503 (m); IV, 832 (w), 805 (w), 783 (w), 768 (s), 746 (s), 696 (s), 658 (w).

Anolobine

Nujol mull: I, 3240 (w); II, 2610 (w); III, 1607 (m), 1512 (w); IV, 850 (w), 833 (w), 807 (w).

Anolobine Hydrochloride

Nujol mull: I, 3330 (m); II, 2800 (s), 2725 (m), 2670 (w), 2640 (w), 2575 (w), 2505 (w); III, 1614 (s), 1589 (w), 1514 (w); IV, 842 (w), 833 (w), 808 (w), 757 (w), 717 (w), 675 (w).

l-ψ-Conhydrine

Nujol mull: 3270 (s), 3110 (s); II, 2750 (s), 2600 (m); IV, 853 (m), 820 (w), 792–746 (w), 745 (w).

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l-ψ-Conhydrine Hydrochloride

Nujol mull: I, 3360 (s), 3195 (w); II, 2730 (s), 2575 (m), 2525 (m), 2430 (m), 2235 (w), 2080 (w); III, 1614 (m), 1599 (m); IV, 842 (w), 823 (w), 733 (w), 720 (w).

Cytisine

Nujol mull: 3280 (w); II, 2805 (w), 2745 (w); III, 1651 (s), 1567 (s), 1552 (s), 1546 (s); IV, 846 (w), 819 (m), 807 (w), 790 (m), 750 (w), 745 (w), 734 (w).

Cytisine Perchlorate

Nujol mull: I, 3090 (m); II, 2765 (m), 2618 (w), 2580 (w), 2410 (w); III, 1650 (s), 1618 (m), 1560 (s); IV, 801 (s), 790 (w), 731 (w), 652 (w), 605 (m).

Regions I and II

Region I includes normal OH and NH stretching vibrations; region II will encompass OH and NH bands modified by salt formation or hydrogen bonding (the region 3000 to 2800 cm.$^{-1}$ has been omitted since it includes the very strong CH stretching vibrations).

In the free bases the normal NH stretching band was observed, in most cases, in the region 3380 to 3205 cm.$^{-1}$. In view of the fact that Marion, Ramsay, and Jones (15) had previously observed that piperidine and some natural products containing this ring system did not exhibit the normal NH stretching band in the spectra of their chloroform solutions, the spectra of two other reduced heterocyclic bases, i.e., pyrrolidine and piperazine were measured in the same solvent. In both cases the normal NH band was absent. This type of phenomenon has also been reported by Chulanovskii (4), who noted that the main NH stretching band of pure diethylamine was shifted to higher frequencies and weakened in carbon tetrachloride solution.

In the majority of cases reported in this paper, salt formation caused a considerable attenuation of the normal NH stretching band (cf. Depas and Khaladji (8)), which was also displaced towards lower frequencies. In nearly all the cases studied, the spectrum of the salt shows a complex series of absorption bands in the region 2800 to 2000 cm.$^{-1}$ which are probably associated with $—NH_2^+$ stretching vibrations. This effect seems to be more apparent in the aromatic series where three or four bands have been observed between 2780 and 2600 cm.$^{-1}$, in all the spectra studied, as well as a variable number of other bands between 2600 and 2000 cm.$^{-1}$. In general, the intensity of the bands in the latter region fell off towards the lower end of the frequency scale. The current investigation demonstrated that out of 17 secondary amine salts studied, 15 showed a band between 2760 and 2690 cm.$^{-1}$. Owing to the complexity of the spectra in this region, however, and the relative scarcity of information available no accurate correlation can be made at the moment.

Region III

In the spectra of all the salts of aliphatic and fully saturated heterocyclic bases investigated by the authors, a definite medium to strong absorption peak was observed near 1600 cm.$^{-1}$ which was invariably absent in the spectra

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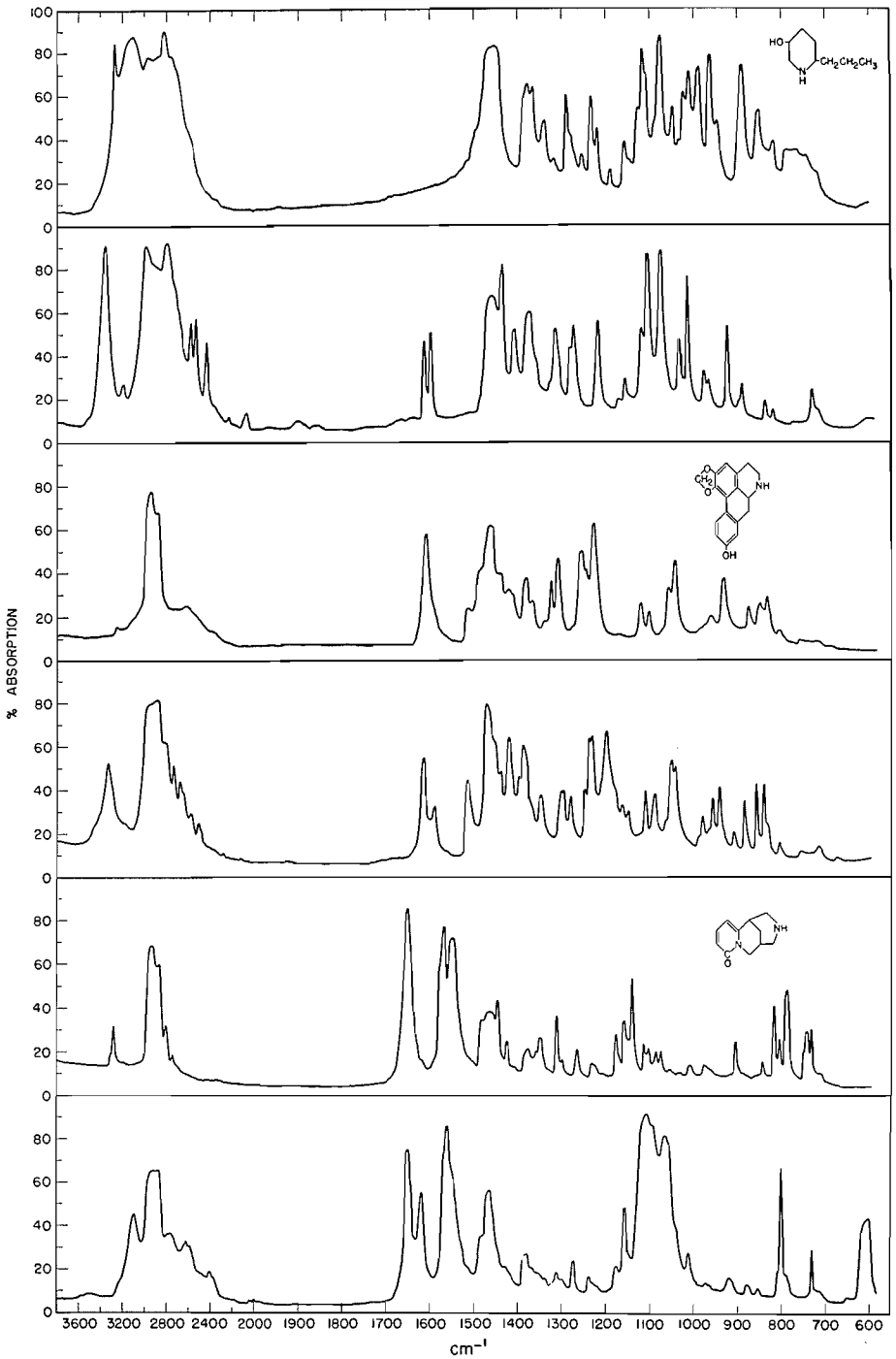

FIG. 1. Infrared absorption spectra of 1, *pseudo*conhydrine; 2, *pseudo*conhydrine hydrochloride; 3, anolobine; 4, anolobine hydrochloride; 5, cytisine; 6, cytisine perchlorate.

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of the corresponding free bases. This band is almost certainly due to deformation vibrations of the protonated secondary amino group. In a few cases two bands are observed in this region as in the spectrum of ψ-conhydrine hydrochloride (1614 and 1599 cm.$^{-1}$) (Fig. 1, curve 2) and in that of 1,2-diethylhydrazine (1597 and 1542 cm.$^{-1}$). In most cases, however, the peak is single as shown in the spectrum of cytisine perchlorate (Fig. 1, curve 6). Aromatic compounds unfortunately absorb in this region owing to the ring vibrations. Nevertheless, by careful comparison of the spectra of the free aromatic base and its salt, it is often possible to pick out the band associated with the $—NH_2^+$ deformation. An example is shown in Fig. 1 where curves 3 and 4 are the spectra of anolobine and its hydrochloride respectively. Whereas the spectrum of the base contains a band at 1607 cm.$^{-1}$ due to the aromatic ring, the spectrum of its hydrochloride shows the same band at 1614 cm.$^{-1}$ and a smaller band at 1589 cm.$^{-1}$ which is attributed to $\rangle NH_2^+$ deformation. In the spectra of the salts of aromatic bases it is noteworthy that the normal aromatic ring vibrations around 1600 cm.$^{-1}$ are greatly reduced in intensity relative to that of the free base. The bands assigned to $—NH_2^+$ deformation are given in Table I.

TABLE I

Salt	Absorption due to $—NH_2^+$ deformation (cm.$^{-1}$)
Dimethylamine hydrochloride	1600
Piperidine hydrochloride	1597
Morpholine hydrochloride	1582
Piperazine hydrochloride*	1552, 1597, 1626
Piperazine hydrochloride monohydrate	1553, 1627
Piperazine perchlorate	1594
Piperazine perchlorate dihydrate	1597
Pyrrolidine picrate	1575
Proline hydrochloride†	1592
N-Phenylglycine hydrochloride†	1600, 1560, 1490
Sarcosine hydrochloride†	1620, 1570
Diethanolamine nitrate	1590
1,2-Diethylhydrazine hydrochloride	1597, 1542
Diphenylamine hydrochloride	1572
N-Ethylaniline hydrochloride	1589
1,2,3,4-Tetrahydroquinoline hydrochloride	1572
5,6-Dihydrophenanthridine hydrochloride‡	1560, 1577
N-Methylanthranilic acid hydrochloride‡	1618, 1542
Methyl *N*-methylanthranilate hydrochloride	1542
Anolobine hydrochloride	1589
ψ-Conhydrine hydrochloride	1614, 1599
Cytisine perchlorate	1618

**Piperazine perchlorate gives the expected absorption, but the hydrochloride apparently behaves somewhat anomalously.*
†Values reported by Randall et al. (16).
‡Probably some coupling of the NH vibrations with the ring vibrations, and the band system is difficult to explain with certainty.

The $—NH_2^+$ deformation frequencies are mostly in the range 1620 to 1560 cm.$^{-1}$ although the salts of some secondary amines absorb at slightly lower wave numbers. For instance, the hydrochlorides of 1,2-diethylhydrazine,

of *N*-methylanthranilic acid, and of its methyl ester show a band at 1542 cm.$^{-1}$.

Both primary amines and their salts absorb in the infrared around 1600 cm.$^{-1}$ whereas tertiary amines and their salts, as well as quaternary ammonium salts, show no absorption in this region. For a number of these the absorption peaks in the following regions: I (4000 to 3000 cm.$^{-1}$), II (2800 to 2000 cm.$^{-1}$), III (1700 to 1500 cm.$^{-1}$), and IV (850 to 600 cm.$^{-1}$) are listed below.

Cyclohexylamine

Liquid: I, 3340 (m), 3275 (m); II, 2675 (w); III, 1604 (m); IV, 840 (s), 773 (s).

Cyclohexylamine Hydrochloride

Nujol mull: I, 3215 (w), 3000 (s); II, 2780 (s), 2735 (m), 2680 (m), 2630 (m), 2580 (m), 2535 (m), 2390 (w), 2075 (m); III, 1625 (m), 1615 (w), 1608 (m), IV, 845 (w).

Cyclohexylamine Perchlorate

Nujol mull: I, 3220 (s); II, 2720 (w), 2675 (w), 2600 (w), 2515 (w); III, 1605 (s); IV, 845 (w).

Trimethylamine

Gas: II, 2775 (s), 2515 (w), 2110 (w); IV, 846–838 (w), 826 (s), 805 (w).

Trimethylamine Hydrochloride

In chloroform: I, 3650 (w), 3420 (w); II, 2575 (s), 2520 (s), 2430 (s), 2380 (s), 2220 (s), 2145 (m).

N-Methylcytisine

Nujol mull: II, 2775 (m), 2730 (w); II, 1660 (s), 1653 (s), 1577 (s), 1556 (s); IV, 808 (s), 741 (w).

N-Methylcytisine Perchlorate

Nujol mull: I, 3575 (w); II, 2715 (w), 2635 (w), 2560 (w); III, 1663 (w), 1647 (s), 1555 (s); IV, 800 (m), 730 (w).

Trimethylphenylammonium Chloride

Nujol mull: III, 1597 (w), 1508 (s); IV, 847 (m), 844 (m), 778 (s), 692 (s).

Tetramethylammonium Iodide

Nujol mull: IV, 717 (w).

It has been assumed that the bands appearing near 1600 cm.$^{-1}$ in the infrared spectra of salts of secondary bases were due to —NH_2^+ deformation vibrations and those in the region 2800 to 2000 cm.^{1} to stretching vibrations of the same group. In order to ascertain whether this assumption was legitimate, the spectrum of *N*-deuteropiperidine deuterochloride (at least 90% deuterated) was compared with that of piperidine hydrochloride (Fig. 2, curves 2 and 4). Deuteration of the amino function considerably modified the spectrum. The intense band system found between 2800 and 2400 cm.$^{-1}$ in the spectrum of piperidine hydrochloride was considerably attenuated in the

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spectrum of the deuterated salt and a number of intense bands appeared between 2400 and 1900 cm.$^{-1}$. These are almost certainly $-ND_2^+$ stretching vibrations (cf. Lenormant (13)). The almost complete disappearance of the medium intensity band[5] near 1600 cm.$^{-1}$ was accompanied by the appearance of two new bands at 1297 cm.$^{-1}$ and 1238 cm.$^{-1}$, one or both of which is probably associated with deformations of the $-ND_2^+$ group, since Randall *et al.* (16) define the range for ND_2 deformations as 1279 to 1193 cm.$^{-1}$. These spectra are shown in Fig. 2. As with the salts there was considerable difference between

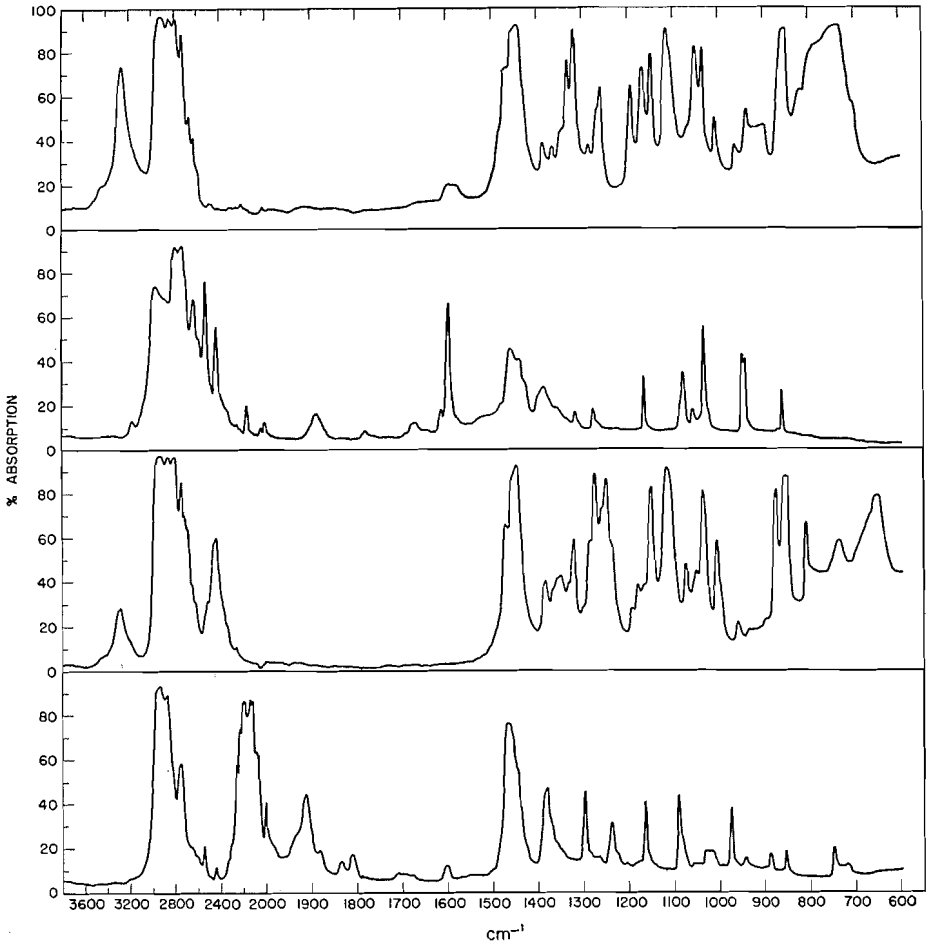

FIG. 2. Infrared absorption spectra of 1, piperidine; 2, piperidine hydrochloride; 3, *N*-deuteropiperidine; 4, *N*-deuteropiperidine deuterochloride.

the spectra of *N*-deuteropiperidine and piperidine. This gave rise to the suspicion that perhaps the exchange of deuterium had affected not only the hydrogen substituted on the nitrogen, but some of the hydrogen substituted

[5]*The fact that the salt was only about 90% deuterated accounts for the small residual band still observed in the spectrum.*

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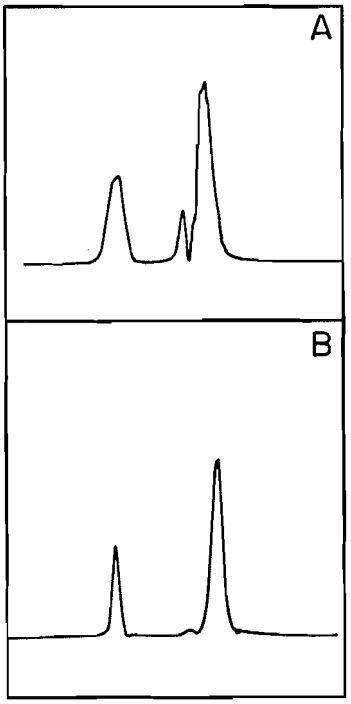

FIG. 3. Nuclear magnetic resonance spectra of A, piperidine; B, *N*-deuteropiperidine.

on the carbon as well. However, an examination of the nuclear magnetic resonance spectra of piperidine and of *N*-deuteropiperidine (Fig. 3) showed that the two peaks due to the hydrogen attached to carbon in the spectrum of piperidine retained the same relative height in the spectrum of *N*-deuteropiperidine. Furthermore, the small peak representing the hydrogen attached to nitrogen in the one spectrum had practically disappeared in the other. Hence, the exchange product was exclusively *N*-deuteropiperidine.

Region IV

Spectral changes on salt formation have been observed in the low frequency region. All the aromatic amine salts referred to in this communication show a weak but very sharply defined band in the region 812 to 803 cm.$^{-1}$. This may be due to NH rocking vibrations of the NH_2^+ group (6) although the fact that it is not present in non-aromatic amine salts renders this assignment dubious. There is also a modification of the aromatic out-of-plane hydrogen deformation bands in this region. The modification consists of an apparent splitting of the band into two with a separation by as much as 10 cm.$^{-1}$, and the splitting is accompanied by a movement of the band pair towards slightly higher frequencies (less than 20 cm.$^{-1}$). As yet, however, too few aromatic secondary amine salts have been studied to consider these last observations as significant.

It can be concluded that secondary amines can be detected by the appearance of a characteristic band in the region 1620 to 1560 cm.$^{-1}$ in the infrared

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spectra of their salts which is invariably absent in the spectra of the bases themselves. The spectra of aromatic secondary bases are complicated by the ring absorption occurring in the same region but in most cases the assignment can still be made. In zwitterionic substances the detection of the secondary amine group is more difficult, and less certain.

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A MANNAN PRODUCED BY SACCHAROMYCES ROUXII[1]

By P. A. J. Gorin[2] and A. S. Perlin

ABSTRACT

The main slime polysaccharide produced by *Saccharomyces rouxii* during the fermentation of D-glucose to D-arabitol is a mannan. Acetolysis of the polymer has afforded di- and tri-saccharides in good yield, but no higher oligosaccharides were produced. The disaccharide is shown by methylation and lead tetraacetate oxidation to be 2-*O*-α-D-mannopyranosyl-D-mannose, establishing the presence of a 1,2-α-linkage in the polysaccharide. On acid hydrolysis the methylated mannan gives mainly 2,3,4,6-tetra-*O*-methyl-D-mannose, 3,4,6-tri-*O*-methyl-D-mannose, and 3,4-di-*O*-methyl-D-mannose; lesser components found are 2,4,6-tri-*O*-methyl-D-mannose and 3-*O*-methyl-D-mannose. The methylation and acetolysis data together suggest an average structural unit consisting of a main chain of D-mannopyranose units containing alternate 1,2- and 1,6-linkages, to which single D-mannopyranose units are attached by 1,2-linkages as side chains; alternatively, 1,2-disaccharide units are attached as side chains by 1,2-linkages to a 1,6-linked main chain.

During the fermentation of D-glucose to D-arabitol by *Saccharomyces rouxii* (14) a slime is produced in the culture medium. The slime was isolated from an active culture filtrate by repeated precipitation with ethanol from water as a light brown powder containing approximately 15% protein. It yielded mainly mannose, on acid hydrolysis, although traces of pentose and another hexose were detected in its hydrolyzate on paper chromatograms. After acetylation, followed by deacetylation of the product, a polysaccharide was obtained which was virtually free of protein and contained only mannose. This purified material had $[\alpha]_D$ +58°, and in common with other mannans formed an insoluble copper complex.

Partial acetolysis of the polysaccharide gave rise to a mixture of mono-, di-, and tri-saccharide acetates which, after saponification, were chromatographed on charcoal (15) and then on cellulose (10). The yields of the di- and tri-saccharide were 10% and 25%, respectively. The disaccharide fraction was amorphous but appeared, from paper chromatographic examination, to be comprised of a single component. It yielded a crystalline octa-*O*-methyl ether, which on hydrolysis gave only crystalline 3,4,6-tri-*O*-methyl-D-mannose (1) and 2,3,4,6-tetra-*O*-methyl-D-mannose, characterized as the phenylhydrazide of the corresponding acid (5). The disaccharide, therefore, was 2-*O*-D-mannopyranosyl-D-mannose; as it has not been crystallized, its possible identity with the crystalline 1,2-mannobiose synthesized by Gakhokidze and Kutidze (6) is not determined. Sodium borohydride reduction of the compound gave crystalline 2-*O*-D-mannopyranosyl-D-mannitol, which, in agreement with the formulated structure, consumed 5 moles of lead tetraacetate per mole (12), producing 1 mole of formaldehyde per mole. The configuration of the glycosidic linkage was established by controlled lead tetraacetate oxidation of the

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[2]*National Research Council of Canada Postdoctorate Fellow, 1955–56.*

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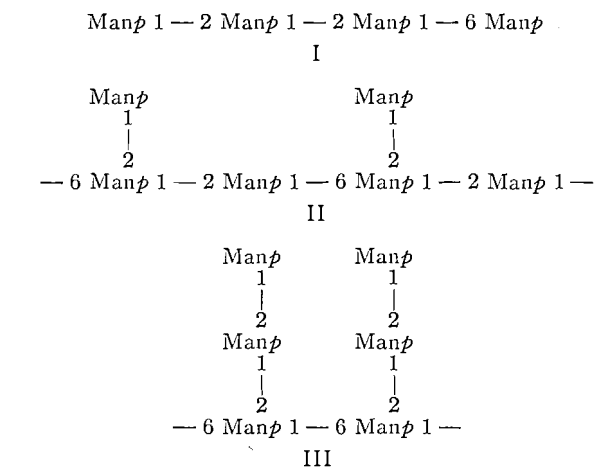
mannobiitol to give 2-*O*-D-mannopyranosyl-D-glyceraldehyde, which was then reduced to sirupy 2-*O*-D-mannopyranosyl-glycerol. The latter proved to be the α-anomer since it and its crystalline hexa-*p*-nitrobenzoate had more positive optical rotations, respectively, than the corresponding β-anomer and its derivative (3), respectively. Therefore the 1,2-linkage in the polysaccharide, as represented by the mannobiose, must possess the α-configuration.

On treatment with lead tetraacetate the mannobiose consumed only traces of oxidant during a reaction time of 30 min., and when oxidation was promoted by addition of potassium acetate (12) 1 mole of formaldehyde per mole was produced within the same period. These results, together with the observed rate of formic acid production and the quantity of reagent consumed, are in complete accord with those anticipated for a 1,2-hexose disaccharide (4, 13), and hence validate the earlier suggestion that lead tetraacetate oxidations may be useful for determining the position of linkage of 1,2-disaccharides as well as of other disaccharide types. Since all but 1,2-reducing disaccharides rapidly consume at least 1 to 2 moles of oxidant in the uncatalyzed reaction (4), the absence of significant lead tetraacetate uptake by the amorphous disaccharide constitutes further evidence of its essential homogeneity.

The mannan was methylated by three treatments with dimethyl sulphate – sodium hydroxide, and the product was then subjected to methanolysis followed by hydrolysis with 80% formic acid at 100° C. Paper chromatographic examination indicated that the hydrolyzate contained five component reducing *O*-methyl ethers. These were separated by chromatography on cellulose and found to be: (*a*) 2,3,4,6-tetra-*O*-methyl-D-mannose, a sirup characterized by conversion to crystalline 2,3,4,6-tetra-*O*-methyl-D-mannonic acid phenylhydrazide (5); (*b*) crystalline 3,4,6-tri-*O*-methyl-D-mannose (1); (*c*) 2,4,6-tri-*O*-methyl-D-mannose, a sirup which was characterized by the fact that on bromine oxidation followed by treatment with methanolic ammonia it gave 2,4,6-tri-*O*-methyl-D-mannonic acid amide (7) and that it was unoxidized by aqueous periodic acid; (*d*) crystalline 3,4-di-*O*-methyl-D-mannose, which was identified from the fact that on lead tetraacetate oxidation it gave mono-*O*-formyl-2,3-di-*O*-methyl-D-arabinose, which in turn was converted to crystalline 2,3-di-*O*-methyl-D-arabonic acid amide; and (*e*) 3-*O*-methyl-D-mannose, characterized since it rapidly consumed 1 mole per mole of lead tetraacetate (13) to yield a material giving a pink color with the *p*-anisidine hydrochloride spray (10) on a paper chromatogram. The ratio of compounds $a:b:c:d$ was approximately 10:7:2:10, and the mono-*O*-methyl ether comprised about 5% of the total. In addition to the 1,2-linkage, already established by isolation of the 1,2-mannobiose, the presence of the 1,6-linkage as a second major type is indicated by the methylation results, and the polysaccharide is shown to possess a highly branched structure. The isolation of 2,4,6-tri- and 3-mono-*O*-methyl-D-mannose in small amounts suggests that the polymer also contains a small proportion of 1,3- and 1,4-linkages but it is possible that these minor components originate through incomplete methylation.

A variety of possible repeating units may be devised using this methylation data. The results of partial acetolysis, however, assist considerably in elimi-

nating certain of these possibilities. As noted above, the acetolysis experiment furnished oligosaccharides having no more than three mannose residues. The trisaccharide fraction, although not yet completely characterized, is known from methylation results to contain only the 1,2-type of glycosidic linkage* making it improbable that the sequence of mannose residues linked 1,2- in the polysaccharide rarely, if ever, exceeds two. Since the yield of trisaccharide is high and because almost 90% of the linkage types encountered are 1,2- and 1,6-, in a ratio of close to 2: 1, then these linkages must frequently occur in a sequence such as represented by (I). To account for the tetra-*O*-methyl (end-groups) and di-*O*-methyl (branch-points) ethers in the proportion in which they are obtained, but not the minor component *O*-methyl ethers, structure (I) is enlarged to give (II) and (III). The latter two types of structural unit are



consistent with all of these data and, accordingly, are suggested as possible average representations for a major proportion of the mannan.

In many respects the slime mannan closely resembles the mannan isolated by Haworth and co-workers from baker's yeast by alkali extraction (7, 8). The acetate of the latter polysaccharide showed $[\alpha]_D$ +59° as compared with the present value of $[\alpha]_D$ +53°. Further, the two methylated mannans on hydrolysis have yielded the same *O*-methyl ethers in approximately the same proportions, with a few minor exceptions. The interpretations of the two sets of data, however, differ somewhat for, in contrast with (II) and (III), all three of the possible formulae advanced by the earlier workers (7) have chiefly 1,2-linkages in the main chain and 1,6-linkages in the side chain. Northcote and Horne (11) have produced evidence that the mannan constitutes part of the cell wall membrane rather than a storage material of the cell. The similarity in the fine structure of the two polysaccharides, therefore, raises the question as to whether the slime mannan is truly extracellular, or represents cell wall matter which is exuded by the active organism or released from spent cells through autolysis.

* *Unpublished data.*

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EXPERIMENTAL

Paper chromatography was carried out on Whatman No. 1 filter paper using *n*-butanol–ethanol–water (40: 11: 19 v/v) as solvent and *p*-anisidine hydrochloride as spray reagent (10). Melting points are uncorrected. Evaporations were carried out under reduced pressure at 40° C. Optical rotations were measured at 27° C.

Preparation of Crude Mannan

A 30% D-glucose solution (5 gal.) containing corn steep liquor (1.1%) and urea (0.53%) was fermented for nine days at 30° C. by *Saccharomyces rouxii*. The cell-free culture medium was concentrated and added to an excess of ethanol and the slime thus obtained was twice reprecipitated by ethanol from water. The final product was isolated as a light brown powder (66 gm.; found: N, 2.62%) which gave on acid hydrolysis mainly mannose, detected on a paper chromatogram. Traces of another hexose and of a pentose were also shown to be present.

Purification of Mannan

The polysaccharide (5.4 gm.), obtained above, was pasted in formamide (50 ml.) and shaken for 18 hr. in a mixture of pyridine (50 ml.) and acetic anhydride (20 ml.). Most of the polysaccharide dissolved and the suspension was filtered off. The filtrate was added to ice water and the precipitate centrifuged off, washed twice with water, and dried. The acetylated material (6.2 gm.) had $[\alpha]_D$ +53° (*c*, 0.75, chloroform).

The acetate (0.89 gm.) was dissolved in chloroform (25 ml.) to which sodium methoxide (0.08 gm. of sodium in 75 ml. of methanol) was added. After one hour the solution was acidified with dilute hydrochloric acid and the precipitate which had formed was filtered off. The polysaccharide was precipitated once from water with an excess of ethanol, centrifuged off, washed with ethanol then ether, and dried. Yield 0.31 gm. The mannan had $[\alpha]_D$ +58° (*c*, 1.0, water) and gave an insoluble copper complex on mixing with Fehling's solution. Only mannose was detected on a paper chromatogram after acid hydrolysis of the product.

2-O-α-D-Mannopyranosyl-D-mannose

The crude polysaccharide (25 gm.) was dissolved by shaking in acetic anhydride (100 ml.) containing sulphuric acid (9 ml.), the temperature of the mixture being kept below 55° C. (2). After further treatment at 35° C. for two days the reaction mixture was filtered and poured into ice water. The mixture was then extracted with chloroform, which was washed with aqueous sodium bicarbonate, then water, dried (magnesium sulphate), filtered, and evaporated to give a solid crust. The latter was dissolved in methanol (200 ml.) to which sodium methoxide (sodium (0.5 gm.) in methanol (20 ml.)) was added. The precipitate which formed was filtered off (14.9 gm.) and the filtrate was evaporated to a solid which was deionized (Amberlites IR-120 and IR-4B) in aqueous solution and evaporated to a solid (3.4 gm.). Both the soluble and insoluble fractions gave spots on a paper chromatogram corre-

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sponding to mono-, di-, and tri-saccharides only, and were combined. A sample of D-mannose was treated with acetic anhydride and sulphuric acid in the same way as the mannan; no reversion products were detectable in significant quantity on a paper chromatogram.

The mixture (14.9 gm.) was partly fractionated on a charcoal column using ethanol–water mixtures (15) and then completely on a cellulose column (10). On the latter column *n*-butanol saturated with water eluted the monosaccharide portion, ethyl acetate – acetic acid – water (9:4:4 v/v) the disaccharide (1.7 gm.), and 70% ethanol the trisaccharide (4.3 gm.).

The disaccharide had $[\alpha]_D$ +40° (*c*, 2.3, water). Behavior of the compound on oxidation with lead tetraacetate (4, 13) eliminated the possibility that the linkage position was 1,3-, 1,4-, 1,5-, or 1,6-. The data obtained, however, was wholly consistent with a 1,2-linkage. Thus, in the uncatalyzed reaction only traces of oxidant were consumed during the first 0.5 hour's reaction time; all except 2-substituted compounds consume 1 to 2 moles per mole within the first 10 min. (4). Also, in the potassium acetate-catalyzed oxidation the compound produced 0.9 mole of formaldehyde per mole in 30 min.; the formic acid production at one, two, three, and five hours, respectively, was 1.5, 2.3, 2.9, and 3.4 moles per mole; and in five hours it produced 0.9 mole of formaldehyde per mole and consumed 6.3 moles of lead tetraacetate per mole. The corresponding data expected (based on the oxidation of 2-*O*-methyl-D-glucose and methyl α-D-mannopyranoside) was 1.0 mole of formaldehyde per mole; 1.8, 2.5, 2.9, and 3.5 moles of formic acid; 1.0 mole of formaldehyde per mole and 6.8 moles of lead tetraacetate per mole.

Methylation of 2-O-α-D-Mannopyranosyl-D-mannose

The disaccharide (0.290 gm.) was methylated four times with dimethyl sulphate – sodium hydroxide as described for the methylation of the mannan (see below) except that during the first treatment the dimethyl sulphate was added before the sodium hydroxide to minimize the possibility of degradation. The product (0.285 gm.) crystallized, was twice recrystallized from *n*-hexane, and had m.p. 43–46° C. and $[\alpha]_D$ +72° (*c*, 0.8, ethanol). Calculated for $C_{20}H_{38}O_{11}$: C, 52.85%; H, 8.43%; —OCH_3, 54.6%. Found: C, 53.25%; H, 8.53%; —OCH_3, 53.2%.

The methylated disaccharide (0.145 gm.) was hydrolyzed by being heated for 18 hr. at 100° C. in formic acid (5 ml.) containing water (0.5 ml.). The reaction mixture was then evaporated to a sirup, dissolved in water, and heated at 100° C. to destroy formate esters. The solution was evaporated to a sirup and the process was repeated twice. The mixture of *O*-methyl sugars was fractionated on a cellulose column. Benzene–ethanol–water (10:1: trace v/v) eluted the tetra-*O*-methyl sugar (0.066 gm.), and benzene–ethanol–water (5:1: trace v/v) the tri-*O*-methyl sugar (0.060 gm.). The tetra-*O*-methyl mannose had $[\alpha]_D$ +8° (*c*, 0.7, water) and was oxidized with bromine to its lactone, which was converted to 2,3,4,6-tetra-*O*-methyl-D-mannonic acid phenylhydrazide, m.p. 180–181° C. Calculated for $C_{16}H_{26}O_6N_2$: C, 56.12%; H, 7.65%. Found: C, 56.30%; H, 7.80%. The tri-*O*-methyl sugar crystallized

and was twice recrystallized from ether to give 3,4,6-tri-*O*-methyl-D-mannose with m.p. 99–101° C. and $[\alpha]_D$ +18° → +8° (constant, 18 hr.) (*c*, 0.7, water). Calculated for $C_9H_{18}O_6$: C, 48.64%; H, 8.16%. Found: C, 48.71%; H, 8.18%. The melting point of each of the above sugars was not depressed by admixture with known specimens, and the correct X-ray diffraction patterns and infrared absorption spectra were given.

2-O-α-D-Mannopyranosyl-D-mannitol

2-*O*-α-D-Mannopyranosyl-D-mannose (0.235 gm.) was dissolved in water (20 ml.) containing sodium borohydride (0.10 gm.) and the solution was left for 18 hr. Acetic acid was added to destroy excess reagent and the solution then treated with Amberlite IR-120 and evaporated to dryness. Boric acid was removed by dissolving the sirup in successive portions of methanol and repeated evaporations of the solution. The product (0.204 gm.) crystallized and was recrystallized twice from methanol–ethanol. It had m.p. 136–137° C. and $[\alpha]_D$ +45° (*c*, 0.8, water). Calculated for $C_{12}H_{24}O_{11}$: C, 41.86%; H, 7.08%. Found: C, 41.66%; H, 7.09%. The alcohol was oxidized with lead tetraacetate in 90% acetic acid containing potassium acetate. After three hours (steady state) 5.2 moles of reagent per mole had been consumed by the carbohydrate and 1.0 mole of formaldehyde per mole liberated. (Calculated: 5.0 and 1.0 moles per mole, respectively).

Methylation of Mannan

The crude mannan (15.0 gm.) was dissolved in water (150 ml.) contained in a three-necked flask. To the vigorously stirred solution and under an atmosphere of nitrogen, sodium hydroxide (2.5 gm.) was added followed by dimethyl sulphate (2.3 ml.). The solution was kept at 0° C. for one hour and then treated with portions of 30% (w/v) sodium hydroxide (75 ml.), followed by dimethyl sulphate (70 ml.) three times. The reaction mixture was heated on a steam bath for two hours to destroy excess dimethyl sulphate, neutralized with acetic acid, and extracted twice with equal volumes of chloroform. The extract was dried (magnesium sulphate), filtered, and evaporated to a light brown solid (9.8 gm.); found: —OCH_3, 43.7%.

Separation of Component O-Methyl-D-mannoses After Hydrolysis of Methylated Mannan

The methylated polysaccharide (4.69 gm.) was refluxed in 2.5% methanolic hydrogen chloride for 18 hr. and the solution was neutralized (silver carbonate), filtered, and evaporated to a brown solid (4.57 gm.). The degraded material was dissolved in formic acid (40 ml.) containing water (10 ml.) and further hydrolyzed by heating of the solution at 100° C. for 48 hr. The solution was evaporated to a sirup which was dissolved in water (50 ml.); the mixture was then heated at 100° C. for three hours to hydrolyze formate esters, the solution being then evaporated to a sirup and the process being repeated four times. The sirupy mixture thus obtained (4.59 gm.) was examined on paper chromatograms and its components separated on a cellulose column as shown in Table I; 3.67 gm. of starting material was used in the separation.

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TABLE I

SEPARATION OF *O*-METHYL-D-MANNOSES

Solvent used in column fractionation	Eluted sugar	Net yield, gm.
Benzene–ethanol–water 10: 1: trace v/v	2,3,4,6-Tetra-*O*-methyl-D-mannose	1.10
	3,4,6-Tri-*O*-methyl-D-mannose	0.68
	2,4,6-Tri-*O*-methyl-D-mannose	0.17
Benzene–ethanol–water 7: 1: trace v/v	3,4-Di-*O*-methyl-D-mannose	0.91
n-Butanol half-saturated with water	3-*O*-Methyl-D-mannose	0.11
Total (81% recovery)		2.97

*2,3,4,6-Tetra-O-methyl-*D*-mannose*

The sirup (0.148 gm.), which had $[\alpha]_D$ +23° (*c*, 4.8, methanol), was oxidized in bromine water. The reaction product was lactonized, and converted to 2,3,4,6-tetra-*O*-methyl-D-mannonic acid phenylhydrazide by the action of phenylhydrazine. Two recrystallizations from benzene gave a product (0.034 gm.) with m.p. 183–184° C. and $[\alpha]_D$ −28° (*c*, 0.8, chloroform). Calculated for $C_{16}H_{26}O_6N_2$: —OCH_3, 36.2%. Found: —OCH_3, 36.0%.

*3,4,6-Tri-O-methyl-*D*-mannose*

The material crystallized spontaneously and was recrystallized twice from ether. It had m.p. 101–103° C. and $[\alpha]_D$ +17° → +8° (constant, 18 hr.) (*c*, 0.9, water) and gave an X-ray diffraction pattern identical with that of an authentic specimen. Calculated for $C_9H_{18}O_6$: C, 48.64%; H, 8.16%. Found: C, 48.64%; H, 8.09%.

*2,4,6-Tri-O-methyl-*D*-mannose*

The sugar had $[\alpha]_D$ +12° (*c*, 1.2, water) and did not consume periodic acid. Calculated for $C_9H_{18}O_6$: —OCH_3, 41.9%; found: —OCH_3, 41.1%. The material was also characterized by conversion to 2,4,6-tri-*O*-methyl-D-mannonic acid amide, m.p. 142–143° C. after two recrystallizations from ethanol–ether–*n*-hexane. Haworth and co-workers (7) report m.p. 145° C.

*3,4-Di-O-methyl-*D*-mannose*

The sugar crystallized and was twice recrystallized from ethyl acetate to give a product with m.p. 70–73° C., which differs from other melting points of this material quoted in the literature (7, 8). Therefore, it (0.086 gm.) was left overnight with lead tetraacetate (0.18 gm.) in acetic acid (15 ml.) containing water (0.3 ml.). Excess lead was then precipitated by the addition of oxalic acid in acetic acid and the solution was filtered. The filtrate was evaporated to a sirup which gave a red-brown spot which moved at a distance of 1.2 compared with 2,3-di-*O*-methyl-L-arabinose on a paper chromatogram. This material (0.088 gm.), presumably 5-*O*-formyl-2,3-di-*O*-methyl-D-arabinose, was dissolved in water (10 ml.) containing bromine (0.2 ml.). After five days excess bromine was aerated off, the solution neutralized (silver carbonate), filtered, treated with Amberlite IR-120, and evaporated to a sirup. The product was heated at 100° C. for three hours to promote lactonization

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and then dissolved in excess methanolic ammonia. The resulting sirup, obtained on evaporation of the solution, crystallized and was recrystallized three times from ethanol–*n*-hexane. Yield 0.033 gm. It had m.p. 156–158° C. and $[\alpha]_D$ −17° (*c*, 0.75, water), and gave an X-ray powder diagram identical with that of 2,3-di-*O*-methyl-L-arabonic acid amide (9). Calculated for $C_7H_{15}O_5N$: C, 43.51%; H, 7.83%. Found: C, 43.55%; H, 7.81%.

3-O-Methyl-D-mannose

The sirup had $[\alpha]_D$ +15° (*c*, 1.2, 50% ethanol), moved at a rate similar to that of 3-*O*-methyl-D-glucose, and gave a brown spot on a paper chromatogram. Calculated for $C_7H_{14}O_6$: $-OCH_3$, 16.0%; found: $-OCH_3$, 15.0%. A portion was oxidized with lead tetraacetate in acetic acid; 1 mole of reagent per mole was consumed immediately, very little more being taken up during the next 30 min. The reaction mixture was then evaporated to a sirup which was dissolved in water and treated with Amberlites IR-120 and IR-4B. The solution was filtered and evaporated to a sirup which on a paper chromatogram gave a pink spot corresponding to a pentose which moved 1.2 times the distance of rhamnose.

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THE CONFIGURATION OF GLYCOSIDIC LINKAGES IN OLIGOSACCHARIDES

I. APPLICATION OF JACKSON AND HUDSON'S OXIDATION METHOD TO REDUCING DISACCHARIDES[1]

By A. J. Charlson[2] and A. S. Perlin

ABSTRACT

Use of glycol-cleavage oxidations to assist in establishing the configuration of biose linkages is considered. The approach is based on degradation of disaccharides to yield compounds of simpler structure, all disaccharides of a given class yielding the same product. Thus, 1,6-D-aldohexopyranose disaccharides on oxidation yield one of two possible trialdehydes, the reducing end-unit being converted to glycolic aldehyde and the non-reducing end-unit to a dialdehyde of a type produced from simpler glycosides. These two compounds differ only in the configuration of the carbon atom which originally constituted the glycosidic center, α-linked disaccharides giving rise to one compound, and β-linked to the other. The relative contribution of the glycosidic center to the optical activity of these oxidation products is thereby enhanced and, accordingly, is expected to promote a large rotational difference between α- and β-compounds. Correlation of a 1,6-disaccharide of unknown configuration with known ones by comparison of specific rotational values should then be possible. Disaccharides having other linkage positions, e.g., 1,2- or 1,4-, are likewise degraded to compounds having fewer asymmetric carbon atoms, which are common to all disaccharides of the same class. The results obtained with disaccharides of established structure are in accordance with the theoretical considerations presented. Experimentally, the procedures are simple and require only small quantities of material.

Recent developments in chromatography (4, 9, 15) have promoted the isolation of an ever-broadening variety of new disaccharides from natural and synthetic sources. Frequently assignment of the configuration of the glycosidic linkage in these disaccharides is based upon the observed equilibrium specific rotation of the particular compound. In the D-series, for example, a high positive rotational value is taken to indicate an α-configuration whereas a β-linkage is suggested by a low positive or negative value. A more definitive assignment of configuration is possible by application of Hudson's Rules of Isorotation (5) provided that a closely-related disaccharide of established structure is known. Other evidence for the type of biose linkage is obtained from the use of specific glycosidases, or from the method employed to synthesize the compound or its anomer and, more recently, from infrared absorption data (1, 7, 16).

The configurations of the anomeric monosaccharide methyl glycosides have been correlated by oxidation with periodate or with lead tetraacetate (6, 8). Thus in the D-series all methyl-α-aldohexopyranosides through cleavage of the 2,3,4-triol group yield the same dialdehyde (I) which has a large positive specific rotation; likewise the β-glycopyranosides all yield a common dialde-

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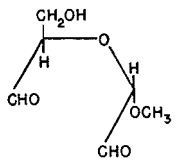
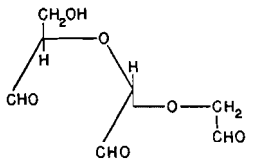
Contribution from the National Research Council of Canada, Prairie Regional Laboratory, Saskatoon, Saskatchewan. Issued as Paper No. 230 on the Uses of Plant Products and as N.R.C. No. 4130. Presented before the 39th Annual Conference of the Chemical Institute of Canada, Montreal, Quebec, 1956.
[2]*National Research Council of Canada Postdoctorate Fellow, 1955–56.*

hyde which differs from I in the configuration at the glycosidic center and possesses a large negative rotation. Alternatively reduction of the dialdehydes according to Smith and van Cleve affords a pair of optical antipodes of equal but opposite rotation, that derived from the α-anomer now having a negative rotation and that from the β-anomer a positive rotation (13). Thus by reducing the number of asymmetric centers in the molecule the relative rotatory power of the glycosidic center is enhanced and a ready correlation achieved between the configuration of the original compound and the specific rotation of the oxidized compound. The present communication considers the possibility of utilizing this approach for determining the configuration of the glycosidic linkage in reducing disaccharides.

Reducing disaccharides, by oxidation with glycol-cleaving agents, yield products which in some respects are similar to the dialdehydes derived from the simple glycosides. For example, D-aldohexopyranose disaccharides having 1,6-linkages are degraded by periodate or lead tetraacetate to a trialdehyde (II) in which the reducing end-unit has been converted to glycolic aldehyde and the glycosidic residue yields a dialdehyde of the type derived from simple glycosides. A 1,4-hexose disaccharide such as cellobiose should be converted by lead tetraacetate to III (11) in which the D-erythrose unit of the reducing end is linked through the 2-position to a dialdehyde of the type derived from β-D-aldohexopyranosides. Maltose, however, should yield a compound which



(I)



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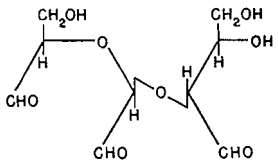

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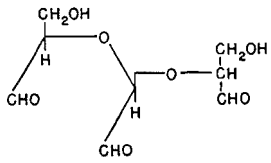

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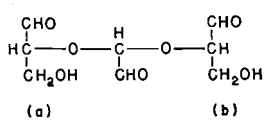
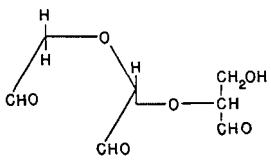


(a) (b)

(V)



(VI)

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differs from III only in that the configuration of the glycosidic center is akin to that of the dialdehyde from an α-D-aldohexopyranoside. Likewise, all D-aldohexopyranose disaccharides in which the reducing end-unit is D-glucose or D-mannose should yield one or other of these oxidation products depending on the configuration of the biose linkage. If D-galactose is the reducing end-unit the product will be III, in which D-erythrose is replaced by D-threose.

The results found experimentally with reducing 1,6- and 1,4-aldohexopyranose disaccharides and related compounds (Table I) agree well with those

TABLE I

SPECIFIC ROTATIONS OF THE PRODUCTS OBTAINED BY GLYCOL-CLEAVAGE OXIDATION OF DISACCHARIDES

Disaccharide	$[\alpha]_D$ disaccharide	Oxidation procedure	$[\alpha]_D$ oxidized disaccharide
Melibiose (1,6α)	+129°	Periodate	+ 79°
Isomaltose (1,6α)	+ 98°*	"	+ 85°
Mannobiose (1,6α)	+ 50°	"	+ 88°
Galactosido-erythritol (1,4α)	+134°	"	+ 79°
Gentiobiose (1,6β)	+ 8°	"	−109°
Mannosido-erythritol (1,4β)	− 39°	"	−106°
Maltose (1,4α)	+130°	Lead tetra-acetate	+ 24°
Glucosido-arabinose (1,3α)	+ 48°	"	+ 19°
Lactose (1,4β)	+ 55°	"	− 78°
Cellobiose (1,4β)	+ 34°	"	− 80°
Glucosido-mannose (1,4β)	+ 47°	"	− 71°
Mannobiose (1,4β)	− 6°	"	− 84°
Glucosido-erythritol (1,2α)	+130°	Periodate	+ 5°
Glucosido-erythritol (1,2β)	− 17°	"	0°
Galactosido-erythritol (1,2β)	+ 7°	"	0°
Glucosido-fructose (1,5α)	− 8°	"	+ 36°
Xylobiose (1,4β)	− 25°	"	+102°

Of the octaacetate.

anticipated. Thus, the specific rotations of oxidized α- and β-1,6-disaccharides differed markedly. Two 1,6-α- compounds, melibiose and isomaltose, yielded products having a strong positive rotation and of approximately the same magnitude. The β-linked disaccharide, gentiobiose, however, yielded a product of opposite rotational sign, and, presumably because the glycolic aldehyde residue contributes little to the over-all rotation, of similar value. A recently-isolated fungal fermentation product, 1-*O*-D-mannopyranosyl-D-erythritol (2), has been assigned a β-configuration from its specific rotation of −39°. This compound was now expected to yield the same trialdehyde as gentiobiose and, in fact, the oxidized products derived from both compounds are found to have strong negative rotations of approximately the same order. On the other hand, 4-*O*-α-D-galactopyranosyl-D-erythritol (3) is degraded to a dialdehyde having approximately the same specific rotation as oxidized 1,6-α-disaccharides. By the same method, 6-*O*-D-mannopyranosyl-D-mannose, $[\alpha]_D$ +52°, is assigned an

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α-configuration since its oxidation product corresponds to that derived from known 1,6-α-compounds.

Three β-1,4-disaccharides—cellobiose, lactose, and 4-*O*-β-D-glucopyranosyl-D-mannose—yielded products having specific rotations all of negative sign and of approximately the same value. On the other hand, the specific rotation of oxidized maltose, being positive, differed greatly from that of the oxidized β-compounds. By treatment with lead tetraacetate, 3-*O*-α-D-glucopyranosyl-D-arabinose, $[\alpha]_D$ +48°, should also yield the same product as maltose, and the observed rotational value after oxidation is in good agreement with this expectation. The specific rotation of the glucosyl-arabinose and that of 6-*O*-α-D-mannopyranosyl-D-mannose are less than that of the known β-disaccharide, lactose, providing instances of the difficulty encountered in assigning configuration on the basis of an equilibrium specific rotation value. 4-*O*-D-Mannopyranosyl-D-mannose (17) had been assigned tentatively the β-configuration from its observed equilibrium rotation of $[\alpha]_D$ −2° and the fact that it was not attacked by an α-mannosidase preparation. Its lead tetraacetate oxidation product has $[\alpha]_D$ −84°, which therefore confirms the 1,4-linkage as of the β-type.

Disaccharides possessing 1,2-linkages are overoxidized by glycol-cleavage agents and therefore cannot be examined by direct oxidation. Overoxidation is avoided, however, if the disaccharide is first reduced to the alcohol (10). Theoretically, therefore, it should be possible to arrive at a pair of α- and β-anomers corresponding to IV in which the reducing end has been degraded to D- or L-glyceraldehyde, depending on the configuration of carbon-2. Three compounds of this type, glycopyranosyl-D-erythritols, were found on oxidation, however, to yield products having zero or very small rotations (Table I). A possible explanation for these apparently anomalous results is that the oxidation products are symmetrical molecules, such as V, in which the rotational contribution of the D-glyceraldehyde unit derived from the non-reducing end (V*a*) should be balanced by the L-glyceraldehyde unit derived from the reducing end (V*b*). A compound possessing two D- or two L-glyceraldehyde units, on the same basis should exhibit significant rotatory power since the contribution of the two substituted trioses would now be additive. In agreement with these considerations, the trialdehyde prepared by oxidation of leucrose (14) (5-*O*-D-glucopyranosyl-D-fructose), theoretically containing two D-glyceraldehyde units, has $[\alpha]_D$ +36°. The observed rotation bears no relation to the original configuration of the disaccharide, however, since the glycosidic center of the oxidation product is not asymmetric. Hence, the method under consideration does not apply for 1,2- (or 1,5-) hexopyranose disaccharides. The products of oxidation, however, are of theoretical interest in that they represent novel illustrations of the relationship between rotatory power and structure.

A pentopyranose disaccharide with a 1,4-linkage or a reduced 1,2-biose should also yield a product containing a glyceraldehyde substituent (VI). This trialdehyde, however, should be stereoisomeric with II, derived from 1,6-hexose disaccharides. Xylobiose (4-*O*-D-xylopyranosyl-D-xylose; $[\alpha]_D$ −25°), for example, which has been assigned the β-configuration, on oxidation should yield the same product as a 1,6-α-hexopyranose disaccharide. The highly

positive specific rotation observed after treatment with periodate ($[\alpha]_D$ +102°) is in good agreement with this expectation, although the numerical value is slightly greater than that found with the oxidized 1,6-α-compounds. Other classes of disaccharides, which on oxidation yield II, e.g., 5- (or 6-) D-pento-furanosyl-pentose (or -hexose) and reduced 2-D-pentopyranosyl-hexose (or -pentose) may likewise be correlated with α- or β-1,6-hexose disaccharides.

Possibly, the configuration of other disaccharide types can be satisfactorily correlated by the method described. A 1,3-pentose disaccharide, for instance, should yield a compound corresponding to III, in which the primary carbinol group of the glyceraldehyde substituent is replaced by hydrogen; if the non-reducing end-unit is pentofuranose or hexopyranose the product should be identical with III. Methyl-pentose units or sugars of the L-series increase the number of possible oxidation products which may be derived from disaccharides, but in several instances the products will be closely similar to those already dealt with.

The data and considerations presented above suggest that glycol-cleavage reactions, already well established as a means for correlating the configuration of glycosidic linkages in glycosides, may also assist in establishing the configuration of biose linkages. However, the reducing end-unit introduces greater complexity and a wide variety of disaccharides must be examined to establish the efficacy of the present approach. The method is not feasible with some classes of compounds, notably 1,2-hexose disaccharides, and is untried with others, such as 1,3-disaccharides. A second method, however, which permits the assignment of configuration to compounds in these two categories, as well as to several other disaccharide types, is described in the succeeding paper of this series. It may be noted also that the configuration of the biose linkage in new disaccharides may be determined in some instances by glycol-cleavage oxidation simultaneously with the linkage position (3, 11).

EXPERIMENTAL

Isomaltose and gentiobiose were prepared from the crystalline octaacetates by deacetylation with sodium methylate (18). The solutions were neutralized with acetic acid, the methanol was evaporated, and the sirups were used directly in the oxidations.

Oxidations with Periodate

In a typical experiment 136 mgm. of melibiose hydrate was dissolved in 5 ml. water and the solution was mixed with 5 ml. of a solution containing 600 mgm. of sodium periodate. Measurements of rotation were made at intervals; the observed rotation was almost constant in four hours at α_D +1.26°, dropping slightly in 24 hr. to +1.13°. Assuming conversion of the melibiose into 72 mgm. of II the specific rotation of the oxidized product was $[\alpha]_D$ +79°.

Oxidations with Lead Tetraacetate

The reactions were carried out at 28°C. in a constant-volume type of Warburg respirometer as described previously (11). In a typical experiment,

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nine manometers were set up and in each flask 1.5 mgm. of maltose in 0.2 ml. of 90% acetic acid was treated with 25 mgm. of lead tetraacetate and 10 mgm. of potassium acetate dissolved in 1.0 ml. of 90% acetic acid. The carbon dioxide evolved during the reaction indicated that approximately one mole of formic acid was liberated in five to six hours' reaction time. The contents of all flasks were then combined and excess lead tetraacetate was destroyed by addition of 0.5 ml. of oxalic acid solution (10%, in acetic acid). The lead oxalate was filtered off and washed with acetic acid and the filtrate was concentrated to dryness at 40°C. Three milliliters of water was added to the residue and the slightly turbid solution was stored at 3°C. for 18 hr. to promote hydrolysis of the formate ester groups (12) (see below), following which the solution was neutralized with lead carbonate and filtered through Celite. The clear filtrate was used for polarimetric measurements (2 dm. tube); α_D +0.17° (initial) → α_D +0.15° (24 hr.; constant value); this corresponded to $[\alpha]_D^{27}$ +23°, assuming that the maltose (13.5 mgm.) had been degraded to 9.9 mgm. of the α-anomer of III.

Experiments in which methyl glycosides were oxidized in the same manner indicated that the loss of oxidation product in this procedure was small. For example, methyl β-D-glucopyranoside gave values of $[\alpha]_D^{27}$ −123° and −132° (see below) as compared with values of −150° (6) and −141° (13) by periodate oxidation.

Oxidations with lead tetraacetate on a larger scale were carried out at 28°C. in glass-stoppered Erlenmeyer flasks. The approximate reaction period to be employed was chosen from results obtained by the small-scale procedures and the degree of oxidation was checked by measurement of lead tetraacetate consumed; five to seven hours appeared to be suitable for all compounds examined, although some oxidations were complete in shorter reaction times. In a typical experiment 51.1 mgm. of lactose hydrate in 10 ml. of 90% acetic acid was treated with a solution of 750 mgm. of lead tetraacetate and 300 mgm. of potassium acetate in 30 ml. of 90% acetic acid. After three hours, titration of a 2.0 ml. aliquot showed that 4.9 moles of lead tetraacetate had been consumed (requires 5.0 moles (3)). An aqueous solution (5.0 ml.) of the oxidation product was prepared as described above and its optical rotation measured: α_D −0.96° (initial) → α_D −1.03° (24 hr.; constant value). The specific rotation, assuming that 48.6 mgm. of lactose hydrate had been oxidized to 33.8 mgm. of III, was $[\alpha]_D$ −76°.

Hydrolysis of Formate Esters Produced During the Oxidation of 1,4-Disaccharides

Maltose, lactose hydrate, and cellobiose were oxidized with lead tetraacetate as described above, *meso*-2,3-butanediol being used in place of oxalic acid to destroy excess oxidant, and with omission of the lead carbonate neutralization step. The hydrolysis rate of the formate esters of each product in aqueous solution was measured polarimetrically, with the following results (initial concentration of sugar, 1%; 2 dm. tube; 27°C.).

These data are similar to those found for hydrolysis of the formate ester groups of di-*O*-formyl-D-erythrose (12).

	Time (hr.)					$[\alpha]_D$
	0.5	5	24	48	72	
Maltose	+1.05°	+0.86°	+0.54°	+0.47°	+0.46°	+31°
Lactose	+0.05°	−0.38°	−0.98°	−1.15°	−1.13°	−77°
Cellobiose	+0.10°	−0.34°	−0.86°	−1.06°	−1.06°	−73°

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THE CONFIGURATION OF GLYCOSIDIC LINKAGES IN OLIGOSACCHARIDES

II. BY DEGRADATION OF REDUCING DISACCHARIDES TO 2-*O*-GLYCOSYL-GLYCEROLS[1]

By A. J. Charlson,[2] P. A. J. Gorin,[2] and A. S. Perlin

ABSTRACT

Reducing aldohexopyranose disaccharides are degraded by employing a series of oxidations and reductions to yield 2-*O*-glycosyl-glycerols, configurations of which are assigned according to Hudson's definition. Maltose, for example, treated with 2 moles of lead tetraacetate gives 2-*O*-α-D-glucopyranosyl-D-erythrose; the latter is reduced to the corresponding alcohol, which is oxidized in turn with 1 mole of lead tetraacetate to give 2-*O*-α-D-glucopyranosyl-L-glyceraldehyde, and a second reduction yields 2-*O*-α-D-glucopyranosyl-glycerol. Cellobiose is converted to 2-*O*-β-D-glucopyranosyl-glycerol by the same sequence of reactions. Other reducing disaccharides containing D-glucopyranose non-reducing end-units may also be degraded to give one or other of these anomeric glycerol-derivatives, the identity of which establishes the configuration of the glycosidic linkage in the original disaccharide. The pair of anomeric 2-*O*-D-galactopyranosyl-glycerols is afforded by the naturally-occurring α-anomer, and the product obtained through degradation of lactose. 2-*O*-D-Mannopyranosyl-D-mannose, obtained after acetolysis of a yeast slime mannan, and 4-*O*-D-mannopyranosyl-D-mannose, from ivory nut mannan, yielded 2-*O*-α- and 2-*O*-β-D-mannopyranosyl-glycerol, respectively, which establishes the configuration of the glycosidic linkages in the disaccharides.

The preceding communication (2) describes the application of Jackson and Hudson's glycoside oxidation method to reducing disaccharides as a means for determining the configuration of glycosidic linkages. Difficulty was encountered in applying the method to some classes of disaccharides, notably 1,2-aldohexose compounds, but this has now been obviated through the development of a second method for determining configuration, which forms the subject of the present paper.

The object of the current approach was to achieve selective degradation of the reducing end-unit of a disaccharide so as to eliminate asymmetry other than that of the non-reducing end-unit of the molecule. Earlier studies (11, 13) had shown that reducing sugars are oxidized very rapidly by lead tetraacetate and are degraded in stepwise fashion, beginning at the α-hydroxy-hemiacetal group. With reducing disaccharides lead tetraacetate effects preferential oxidation of the reducing end-unit; cellobiose (I), for example, was degraded with 2 moles of the reagent to yield 2-*O*-β-D-glucopyranosyl-D-erythrose (II) (1). After reduction, the tetritol derivative was converted by oxidation with 1 mole of lead tetraacetate to 2-*O*-β-D-glucopyranosyl-L-glyceraldehyde (III), advantage being taken of the considerably greater reactivity of polyols relative to glycosides (4, 5). The L-glyceraldehyde unit was then reduced

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[2]*National Research Council of Canada Postdoctorate Fellow, 1955–56.*

affording 2-*O*-β-D-glucopyranosyl-glycerol (IV). In this manner, therefore, all asymmetric centers originally present in the reducing end-unit of cellobiose were eliminated, the compound being converted to a simple glycoside.

By the same sequence of reactions as those used with cellobiose, maltose has now been degraded to give 2-*O*-α-D-glucopyranosyl-glycerol. The two D-glucopyranosyl-glycerols constitute an α, β-anomeric pair of D-glycosides of which, by Hudson's Rules (7), the member having the highest positive rotation possesses the α-configuration. Since the glycoside derived from maltose has $[\alpha]_D$ +121°, and from cellobiose $[\alpha]_D$ −30° (Table I), the isolation of these compounds provides an independent confirmation of the assigned linkage-configurations in maltose and cellobiose. Similarly it is possible to determine the configuration of other disaccharides containing a non-reducing D-glucopyranose end-unit which, on degradation, yield one or other of the glycerol-glucosides.

Degradation of lactose by the method described above has furnished 2-*O*-β-D-galactopyranosyl-glycerol, $[\alpha]_D$ −2°. A different 2-*O*-D-galactopyranosyl-glycerol, $[\alpha]_D$ +165°, has been isolated from natural sources (8, 9, 15). By definition, the latter of this anomeric pair is the α-compound, which therefore confirms the configuration of the naturally-occurring product and provides an additional proof for the β-linkage in lactose. As in the related D-glucose series, these two D-galactosides constitute a basis for the definitive assignment of linkage-configuration in disaccharides containing D-galactopyranose non-reducing end-units.

Two mannose-containing disaccharides isolated by fragmentation of polysaccharides proved suitable for preparation of the requisite pair of anomeric 2-*O*-D-mannopyranosyl-glycerols. One of these disaccharides was 2-*O*-D-mannopyranosyl-D-mannose, which was obtained after acetolysis of a yeast slime polysaccharide produced by *Saccharomyces rouxii* (3). The compound was reduced to the corresponding alcohol, 2-*O*-D-mannopyranosyl-D-mannitol (3), which was oxidized with 3 moles of lead tetraacetate; the oxidation product was then reduced giving 2-*O*-D-mannopyranosyl-glycerol, $[\alpha]_D$ +51°. The second mannobiose used was 4-*O*-D-mannopyranosyl-D-mannose, a product of the partial hydrolysis of ivory nut mannan, which was identical with the 1,4-compound isolated by Whistler and Stein through degradation of guaran (18). After two successions of oxidation and reduction, as already described for other 1,4-disaccharides, the mannobiose afforded 2-*O*-D-mannopyranosyl-glycerol, $[\alpha]_D$ −43°. The latter compound is therefore the β-anomer, confirming the configuration assigned the 1,4-linkage in the guaran polysaccharide and thereby establishing also the 1,4-β-linkage in ivory nut mannan. On the other hand, the first mannosyl-glycerol must be the α-anomer, which establishes the configuration of the 1,2-linkage in the yeast mannan.

The properties of the glycosyl-glycerols are summarized in Table I. Some of the compounds have not been obtained as yet in crystalline form but have been characterized as the derived crystalline benzoates or *p*-nitrobenzoates. The X-ray diffraction pattern and infrared absorption spectrum of each compound were distinctive, which served further to differentiate between

TABLE I

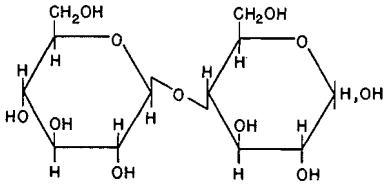
PROPERTIES OF 2-*O*-D-GLYCOSYL-GLYCEROLS AND DERIVATIVES

Compound	Melting point	$[\alpha]_D^{27*}$	$[M]_D^{27}$	2B	
				Found†	Calc.‡
2-*O*-α-D-Glucopyranosyl-glycerol	Sirup	+121°	+30730		
2-*O*-α-D-Glucopyranosyl-glycerol hexabenzoate	137°–138°C.	+96°		+23110	+24220
2-*O*-β-D-Glucopyranosyl-glycerol	163°	−30°	−7620		
2-*O*-β-D-Glucopyranosyl-glycerol hexabenzoate	145°–146°C.	−4°			
2-*O*-α-D-Galactopyranosyl-glycerol	128.5°C. (15)	+165°(15)	+41910	+41400	+38050
2-*O*-β-D-Galactopyranosyl-glycerol	126°–127°C.	−2°	−500		
2-*O*-α-D-Mannopyranosyl-glycerol	Sirup	+51°	+12950		
2-*O*-α-D-Mannopyranosyl-glycerol hexa-*p*-nitrobenzoate	101°–103°C.	−62°		+2030	+1830
2-*O*-β-D-Mannopyranosyl-glycerol	Sirup	−43°	−10920		
2-*O*-β-D-Mannopyranosyl-glycerol hexa-*p*-nitrobenzoate	112°–114°C.	−113°			

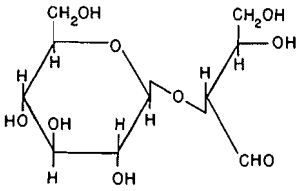
* *Of the glycosyl-glycerols, in water; of the derivatives, in chloroform.*
† *Sum of the molecular rotations* $[M]_D$ *for the α- and β-D-glycosyl-glycerols; temperature 27°C.*
‡ *Sum of the molecular rotations* $[M]_D$ *for the α- and β-methyl-D-glycosides; temperature 20°C.*
Values taken from Ref. 14

anomers. Yields were generally high but in several instances, as when the non-reducing end-unit was prone to a relatively rapid oxidative attack, for example, with mannosides and galactosides, the compound had to be separated from by-products by chromatography on cellulose (6).

Results presented above show that 1,2- and 1,4-aldohexose disaccharides may readily be degraded to furnish one or other of two possible 2-*O*-glycosyl-glycerols, the identity of which determines the configuration of the linkage in the original disaccharide. From the known reactions of disaccharides with lead tetraacetate (1, 12) and by analogy with the present results, it is clear that the current method should be equally suitable for several other classes of disaccharides.



(I)



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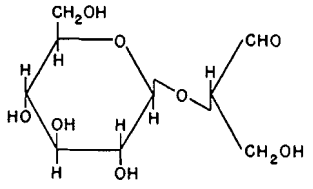

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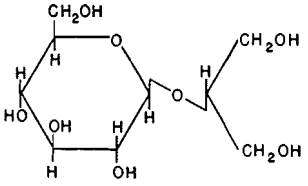

(IV)

EXPERIMENTAL

Optical rotations were measured at 27° C. Melting points are uncorrected. Chromatography was carried out on Whatman No. 1 filter paper using *n*-butanol–ethanol–water (40: 11: 19 v/v) as solvent. R_{gal} and R_{man} denote the distance moved on a paper chromatogram relative to galactose and mannose respectively. Non-reducing sugars were detected on paper chromatograms by the ammoniacal silver nitrate spray (10). Solutions were evaporated under reduced pressure at 40°C. Infrared absorption spectra were prepared by the potassium bromide window technique (16).

*2-O-β-*D*-Galactopyranosyl-glycerol*

Lactose (3.1 gm.) dissolved in water (8 ml.) was taken up in acetic acid (450 ml.), and lead tetraacetate (8.0 gm.; 2.1 molar equivalents) was added to the stirred solution. After two hours' reaction time, oxalic acid (1.4 gm.) in acetic acid (14 ml.) was added and stirring was continued for 30 min. The lead oxalate was filtered off and the filtrate was concentrated to dryness. The

residue, dissolved in water (30 ml.), was deionized with Amberlite IR-120 and reduced with sodium borohydride (1 gm.). From the reduction product, 2-*O*-β-D-galactopyranosyl-D-erythritol (R_{gal} 0.75; 1.1 gm.) was crystallized using aqueous methanol. After two further recrystallizations from the same solvent, the product had m.p. 184°–187°C. and $[\alpha]_D$ +7° (*c*, 1.1, water). Calculated for $C_{10}H_{20}O_9$: C, 42.25%; H, 7.09%. Found: C, 42.03%; H, 7.12%.

2-*O*-β-D-Galactopyranosyl-D-erythritol (0.92 gm.) was oxidized with lead tetraacetate (1.5 gm.; 1.05 molar equivalents) in acetic acid (170 ml.) containing water (3 ml.) for four hours. The mixture was worked up as described above and reduced with aqueous sodium borohydride (0.3 gm.). A methanolic solution of the reduction product on treatment with ethanol deposited crystals of unchanged 2-*O*-β-D-galactopyranosyl-D-erythritol (0.18 gm.). The mother liquor was concentrated to a sirup (0.69 gm.) which contained 2-*O*-β-D-galactopyranosyl-glycerol, 2-*O*-β-D-galactopyranosyl-erythritol, and some over-oxidation products (detected on a paper chromatogram). Pure 2-*O*-β-D-galactopyranosyl-glycerol (0.33 gm.) was isolated on a cellulose column (6) using *n*-butanol half-saturated with water as the mobile phase. The glycerol derivative was crystallized from ethanol–methanol and after recrystallization from the same solvent it had m.p. 126–127°C. and $[\alpha]_D$ −2° (*c*, 1.2, water). Galactose and glycerol were produced on acid hydrolysis (detected on a paper chromatogram). Calculated for $C_9H_{18}O_8$: C, 42.52%; H, 7.14%. Found: C, 42.56%; H, 7.15%. Naturally-occurring 2-*O*-α-galactopyranosyl-glycerol moved at the same rate as the β-compound on a paper chromatogram (R_{gal} 1.1) but it depressed the melting point markedly. The α- and β-glycerols gave different X-ray powder diagrams and different infrared absorption spectra.

2-O-α-D-Glucopyranosyl-glycerol

2-*O*-α-D-Glucopyranosyl-D-erythritol (1.2 gm.), obtained by deacetylation (19) of 2-*O*-α-D-glucopyranosyl-D-erythritol heptaacetate (1), was oxidized with lead tetraacetate (1.9 gm.; 1.0 molar equivalents) in acetic acid (300 ml.) containing water (5 ml.) for six hours. The product was isolated by the procedure described above and was reduced with aqueous sodium borohydride. The resultant sirup, which showed an intense spot (R_{gal} 1.3) and a faint spot (R_{gal} 0.9) on a paper chromatogram, was purified on a cellulose column using *n*-butanol half-saturated with water as the mobile phase. The major product (0.75 gm.), obtained as a sirup from the column, gave glucose and glycerol on acid hydrolysis (detected on a paper chromatogram) and had $[\alpha]_D$ +121° (*c*, 1.0, water). Its infrared absorption spectrum differed from that of 2-*O*-β-D-glucopyranosyl-glycerol.

2-O-α-D-Glucopyranosyl-glycerol Hexabenzoate

Benzoyl chloride (0.4 ml.) dissolved in chloroform (0.4 ml.) was slowly added to a mixture of 2-*O*-α-D-glucopyranosyl-glycerol (0.11 gm.), pyridine (0.5 ml.), and chloroform (0.5 ml.) at −10°C. The reaction mixture was kept at −10°C. for 18 hr. and then at 0°C. for five hours. Chloroform (20 ml.) was then added, and the solution was washed successively with ice-cold dilute sulphuric acid, aqueous potassium bicarbonate, and water, and was dried over

sodium sulphate. Evaporation of the chloroform left a sirup which crystallized slowly from methanol – petroleum ether (b.p. 80–100°C.) (yield 0.28 gm.). The material was recrystallized twice from ethanol; m.p. 137°–138°C., $[\alpha]_D$ +96° (*c*, 0.9, chloroform). Calculated for $C_{51}H_{42}O_{14}$: C, 69.69%; H, 4.82%. Found: C, 70.12%; H, 4.78%.

*2-O-β-*D*-Glucopyranosyl-glycerol Hexabenzoate*

Crystalline 2-*O*-β-D-glucopyranosyl-glycerol (1) (0.062 gm.) was benzoylated with benzoyl chloride (0.2 ml.) in pyridine (0.25 ml.) and chloroform (0.45 ml.) as described for the α-anomer. The hexabenzoate was isolated by the above procedure and was crystallized from ethanol (yield 0.13 gm.). After recrystallization from ethanol the product had m.p. 145°–146°C. after softening at 137°C., $[\alpha]_D$ −4° (*c*, 1.1, chloroform). Calculated for $C_{51}H_{42}O_{14}$: C, 69.69%; H, 4.82%. Found: C, 69.68%; H, 4.77%.

*4-O-β-*D*-Mannopyranosyl-*D*-mannose*

The mannan (43 gm.) obtained by the alkali extraction of ivory vegetable chips was dissolved in water (400 ml.) containing sodium hydroxide (20 gm.). Hydrochloric acid (10 *N*) (75 ml.) was added, the milky suspension heated at 80°C. for four hours, the solution neutralized (sodium bicarbonate) and then transferred to a charcoal column (17). The column was washed with water to remove monosaccharides and then with 2% aqueous ethanol, which eluted the disaccharide fraction. The eluate was evaporated to a sirup (1.47 gm.) which was deionized (Amberlites IR-120 and IR-4B) in an aqueous solution. Crystallization of the sugar took place from *n*-butanol–methanol–water and it was recrystallized from the same solvent (yield 640 mgm.). It had m.p. 188°–193°C., undepressed on admixture with an authentic specimen, and $[\alpha]_D$ −6° (*c*, 1.5, water; equil. value). Calculated for $C_{12}H_{22}O_{11}$: C, 42.10%; H, 6.48%. Found: C, 41.97%; H, 6.50%.

*2-O-β-*D*-Mannopyranosyl-*D*-erythritol*

The above mannobiose (310 mgm.), dissolved in water (1 ml.), was taken up in acetic acid (50 ml.) and lead tetraacetate (800 mgm.; 2.0 molar equivalents) was added. After 18 hr. reaction time the lead was precipitated by addition of oxalic acid in acetic acid. The precipitate was removed by filtration and the filtrate was evaporated to dryness. The residue was dissolved in water (25 ml.) and added to sodium borohydride (250 mgm.) in water (25 ml.). After two hours, excess reagent was destroyed and the product was obtained by the usual procedure. The sirupy product (260 mgm.) had $[\alpha]_D$ −35° (*c*, 2.6, methanol).

*2-O-β-*D*-Mannopyranosyl-*D*-erythritol Hepta-p-nitrobenzoate*

The mannosyl-erythritol (23 mgm.) was heated at 80°C. for 30 min. in pyridine (1 ml.) containing *p*-nitrobenzoyl chloride (160 mgm.). The reaction mixture was added to aqueous potassium bicarbonate and after 30 min. stirring the precipitate was filtered off. The material was recrystallized twice from acetone–ethanol. Yield 45 mgm., m.p. 116°–118°C., $[\alpha]_D$ −106° (*c*, 0.4,

acetone). Calculated for $C_{59}H_{41}O_{30}N_7$: C, 53.36%; H, 3.11%. Found: C, 53.30%; H, 2.91%.

2-O-β-D-Mannopyranosyl-glycerol

The mannosyl-erythritol (255 mgm.) was dissolved in an acetic acid – water mixture (40 ml.: 0.5 ml.) and lead tetraacetate (400 mgm.; 1.0 molar equivalent) added. Using conditions similar to those described above, the mannosyl-L-glyceraldehyde was isolated and reduced with aqueous sodium borohydride. The reaction product (236 mgm.) on a paper chromatogram gave two spots of roughly equal intensity having R_{gal} 0.9 and 1.2, respectively, the faster moving material corresponding to the required glycerol derivative. The latter was isolated from the mixture by fractionation on a cellulose column (solvent: *n*-butanol saturated with water). Yield 89 mgm., $[\alpha]_D$ −43° (*c*, 1.4, water). Acid hydrolysis of the material gave a mixture of mannose and glycerol (detected on a paper chromatogram).

2-O-β-D-Mannopyranosyl-glycerol Hexa-p-nitrobenzoate

The glycerol derivative (21 mgm.) was heated for 30 min. at 80°C. in pyridine (0.8 ml.) containing *p*-nitrobenzoyl chloride (136 mgm.). The product was isolated as described above and recrystallized twice (acetone–ethanol) to m.p. 112°–114°C. (depressed to 105°C. on admixture with the corresponding α-isomer). Yield 54 mgm., $[\alpha]_D$ −113° (*c*, 0.9, chloroform). Calculated for $C_{51}H_{36}O_{26}N_6$: C, 53.32%; H, 3.16%. Found: C, 53.39%; H, 3.13%.

2-O-α-D-Mannopyranosyl-glycerol

2-*O*-α-D-Mannopyranosyl-D-mannitol (0.27 gm.) was oxidized with lead tetraacetate (1.01 gm.; 3.0 molar equivalents) in acetic acid (50 ml.) containing water (1 ml.). After three hours the solution was treated with oxalic acid in acetic acid to remove the lead in solution. The mannosyl-D-glyceraldehyde was isolated as described previously and reduced by the usual method with aqueous sodium borohydride to 2-*O*-α-D-mannosyl-glycerol (158 mgm.); $[\alpha]_D$ +51° (*c*, 1.5, water). The sirupy product gave a single spot R_{man} 1.0 on a paper chromatogram. The mixture produced by acid hydrolysis of the product corresponded on a paper chromatogram to mannose and glycerol.

2-O-α-D-Mannopyranosyl-glycerol Hexa-p-nitrobenzoate

2-*O*-α-D-Mannopyranosyl-glycerol (40 mgm.) was converted to the *p*-nitrobenzoate using the same conditions as for the preparation of the β-anomer. Three recrystallizations from acetone–ethanol gave a product (46 mgm.) with m.p. 101°–103°C. and $[\alpha]_D$ −62° (*c*, 0.8, chloroform). Calculated for $C_{51}H_{36}O_{26}N_6$: C, 53.32%; H, 3.16%. Found: C, 53.25%; H, 3.20%. The infrared absorption spectrum differed from that of the β-anomer nitrobenzoate.

ACKNOWLEDGMENT

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PREPARATION AND TOXICITY OF SOME ALKYL THIOPYROPHOSPHATES[1]

By R. A. McIvor, G. D. McCarthy, and G. A. Grant

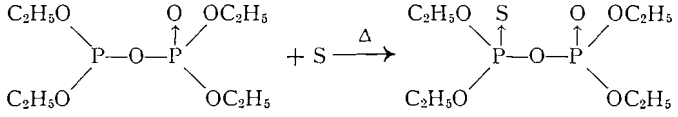
ABSTRACT

Several methods have been investigated for the synthesis of tetraalkyl thiopyrophosphates, including one that can be carried out very rapidly with high yield. Purification of these compounds proved exceedingly difficult, because they were sensitive to traces of acids or bases, and probably to inorganic salts at temperatures above 70° C. All methods investigated yield only the thiono isomer, there being no evidence for the corresponding P—S—P isomer. Toxicological studies do not support the results reported by Fiszer and workers. None of the compounds is more toxic intravenously than tetraethyl pyrophosphate. The synthesis of several other related compounds for infrared study is reported.

INTRODUCTION

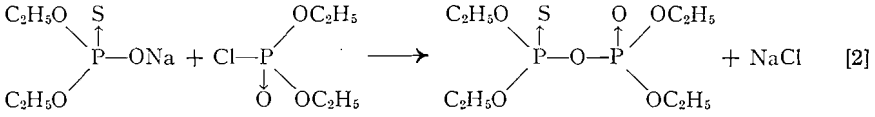
This work was undertaken to clarify the structure of the thiopyrophosphates. Although these compounds had been reported in the literature previously, it was not clear whether they could be obtained in different isomeric forms, or which of the possible isomers was obtained by the various synthetic methods.

Tetraethyl thiopyrophosphate was first reported in 1931 by Arbusov and Arbusov (1), who prepared it in 20% yield by the addition of sulphur to diethyl (diethyl phosphoryl) phosphite.



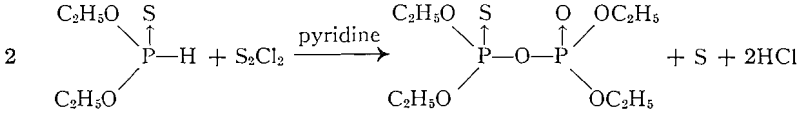
[1]

It has since been prepared by Schrader (34), Hall (18), Kosolapoff (26), and by Fiszer *et al.* (14) in 30 to 70% yields by reacting sodium diethyl phosphorothioate with diethyl phosphorochloridate.



[2]

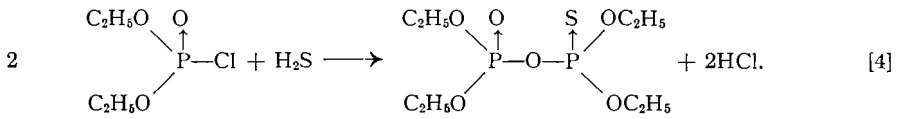
Harman and Stiles (19) prepared this compound by adding a sulphur chloride to diethyl hydrogen phosphonate in the presence of pyridine.



[3]

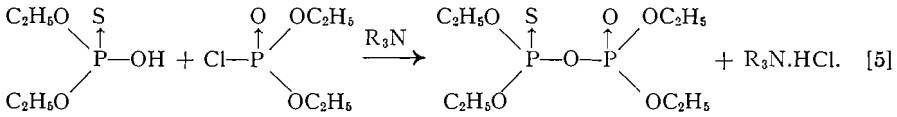
[1]*Manuscript received August 14, 1956.*
Contribution from the Defence Research Chemical Laboratories, Ottawa, Ont. Issued as D.R.C.L. Report No. 201A. Presented in part at the 24th ACFAS Conference, Montreal, Nov. 3, 1956.

Another method used by Fiszer *et al.* (14) was the addition of H_2S to diethyl phosphorochloridate:



[4]

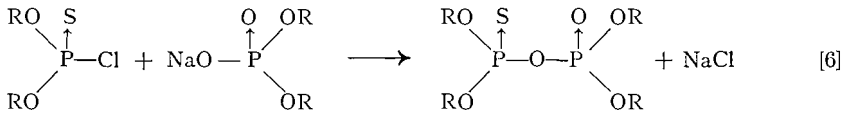
Finally, Arbusov *et al.* (2) recently reported the preparation of this compound in good yield as follows:



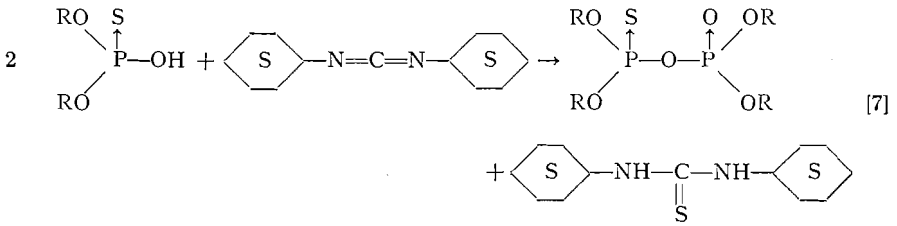
[5]

RESULTS

One or more members of this series have been prepared by methods [3], [4], and [5] mentioned in the introduction, and the following previously unreported methods have been investigated. For all methods, small amounts of impurities,



[6]



[7]

or slight changes of reaction conditions, produce large variations in yields, especially if conventional distillation is attempted.

Method [3] was used for the ethyl compound only. The product decomposed on distillation.

Method [4] gave occasional good results with the ethyl and *n*-propyl compounds, giving approximately 50% yields after distillation. On other occasions, the product completely decomposed on distillation. At no time was a reasonably satisfactory crude product isolated.

Method [5] proved to be the easiest to carry out, and gave crude products of 90 to 95% purity, which could not be distilled directly. The crude yields were as high as 80% based on phosphorus trichloride. It was successful for all tetraalkyl thiopyrophosphates tried. The chief by-product is the *OOS*-trialkyl phosphorothioate.

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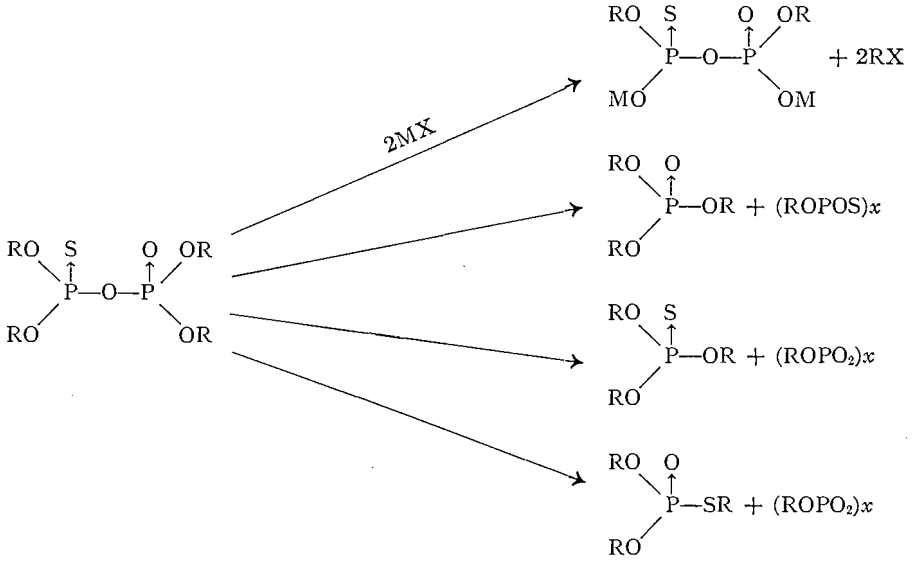
Method [6] gave yields up to 70% of tetraethyl thiopyrophosphate but the starting materials were more difficult to obtain. Considerable effort was required to find the appropriate conditions for this reaction, which is best carried out without solvent, although a trace of tertiary base is essential. This method also gives tetraethyl pyrophosphate and tetraethyl dithionopyrophosphate as by-products in quite appreciable yield, and gave poor results with other alkyl groups.

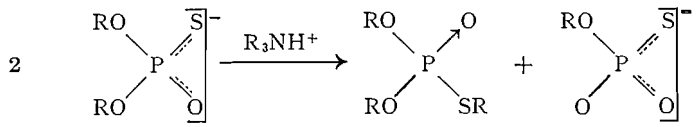
Method [7] gave a mixture of products when heated. At room temperature no reaction took place.

Attempts to synthesize tetraethyl thiopyrophosphate by heating diethyl phosphorothiocyanidate (33) with sodium diethyl phosphite failed. Triethyl phosphate and sodium thiocyanate were the products identified. Also unsuccessful was the attempted synthesis by heating diethyl hydrogen phosphate with triethyl phosphorothionate. In this case, the phosphorothionate distilled unchanged, and at higher temperatures the diethyl hydrogen phosphate pyrolyzed, producing triethyl phosphate.

It has been found that traces of acid (from hydrolysis) or salts, such as triethylamine hydrochloride, or triethylamine salts of the hydrolysis acids, all induce decomposition of the thiopyrophosphates at temperatures above 80° C. The chief reactions taking place seem to be those of disproportionation and salt catalyzed dealkylation (39).



It has been found that when traces of salt are present, a disproportionation reaction occurs on the heating of dialkyl phosphorothioic acids. The yield of the products is about 25%, so other reactions probably occur.



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Traces of salts were almost impossible to remove by filtration or washing, either because of postprecipitation due to incomplete reaction, or by solution with dissociation. Sodium chloride presented the least difficulty in this respect, but was formed in such a finely divided state that filtration was difficult and prolonged, offering an opportunity for hydrolysis. It was eventually found possible to remove salts and acids by passing the material in chloroform solution through a short alumina column. When elution was complete, the compound was stripped of lower boiling materials and distilled at 0.5 to 1 mm. pressure with only slight decomposition. The crude material could usually be partially purified by distillation on a falling-film evaporator. Decomposition was slight, but no separation from phosphorus triesters was achieved.

Paper chromatography was used to assess the purity of thiopyrophosphates. Also by the method used, approximately 1 gram of sample can be separated into its components. Most samples, depending on methods of preparation, resolve into several spots, ranging in number from two to seven. These spots correspond to the two hydrolysis acids, tetraalkyl pyrophosphate, tetraalkyl monothionopyrophosphate, tetraalkyl dithionopyrophosphate, and various trialkyl phosphates and phosphorothioates. Samples stored for several months showed appreciable decomposition. The paper chromatographic technique will be described elsewhere (11).

Infrared spectra have conclusively shown that the thiono isomer is obtained from all methods investigated, and no evidence for a P—S—P isomer has been obtained, even as a transient intermediate, whenever there is a possibility of forming a thiono isomer. These studies have been reported separately (28). The chief points of evidence are:

1. All preparations have a strong P → O band near 7.75 μ (1290 cm.$^{-1}$), the position calculated for the thiono isomer by the method of Bell *et al.* (7), rather than near 7.85 μ (1275 cm.$^{-1}$) as would be expected for the P—S—P isomer and trialkyl phosphorothiolates.

2. All preparations have a P—O—P band near 10.5 μ (950 cm.$^{-1}$).

3. All of these compounds have a band between 12 and 13 μ (770–835 cm.$^{-1}$) attributed to P → S.

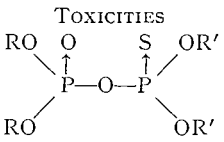
4. None of these compounds has a band beyond 18 μ (555 cm.$^{-1}$) in the position expected for a P—S—P linkage. Crude products occasionally have bands in the 16–18 μ (555–625 cm.$^{-1}$) region at the same wavelength as those in authentic samples of the corresponding trialkyl phosphorothiolates. The intensities of these bands can be directly correlated with the intensities of weak P → O bands in the 7.85 μ (1275 cm.$^{-1}$) region, and these bands become less intense as purer samples are obtained.

The toxicity studies of the best samples of these compounds are reported in Table I, compared with those reported by Fiszer *et al.* (14).

A number of other related compounds were prepared for infrared studies. Most were prepared by conventional methods.

TABLE I

TOXICITIES



R	R′	LD_{50} in mgm./kgm. Mice intraperitoneally	Mice intramuscularly	Mice intravenously	Mice and rats intramuscularly (14)
CH_3	CH_3	*ca.* 1.4			0.25
CH_3	C_2H_5	*ca.* 1.0			
C_2H_5	CH_3	*ca.* 1.8			1.0
C_2H_5	C_2H_5	0.94	0.5	0.3	0.055
n-C_3H_7	n-C_3H_7	7.93	4.41	3.25	
i-C_3H_7	i-C_3H_7	*ca.* 25			50
n-C_4H_9	n-C_4H_9	*ca.* 60			0.25

Tetraethyl pyrophosphate, tetrapropyl pyrophosphate, and tetraethyl dithionopyrophosphate were prepared by the method of Toy (37). Diethyl and dimethyl hydrogen phosphonothioates and *OOS*-trimethyl phosphorodithioate were obtained as described by Kabachnik and Mastryukova (21). Dialkyl phosphorodithionic acids and most dialkyl phosphorochloridothionates were prepared as described by Kabachnik and Mastryukova (22), Fletcher *et al.* (16), and Bacon and LeSuer (6). *SS*-Bis(diethyl phosphorothionyl)-*O*-ethyl phosphorotrithioate was obtained as a by-product of this reaction. Dialkyl phosphorochloridothionates were also prepared by three other methods (8, 15, 32), the first of which was also used for alkyl phosphorodichloridothionates. Attempts to convert triethyl phosphorothionate to diethyl phosphorochloridothionate with phosgene, thionyl, and sulphuryl chlorides failed.

Dialkyl hydrogen phosphonates, and dialkyl phosphorochloridates were prepared according to the procedure of Fiszer and Michalski (13), while the corresponding phosphorothioic acids were obtained by the addition of sulphur to the hydrogen phosphonate (2).

It was found that much better yields, and almost as pure products, could be obtained if the dialkyl hydrogen phosphonates and dialkyl phosphorochloridates were not distilled.

Sodium diethyl phosphate and sodium dimethyl phosphate were prepared by the partial alkaline hydrolysis of the trialkyl phosphates. The higher homologues were prepared by neutralization of the appropriate dialkyl phosphoric acid, obtained by aqueous hydrolysis of the corresponding dialkyl phosphorochloridates.

SSS-Triethyl phosphorotrithioate and triethyl phosphorotetrathioate were synthesized by the addition of phosphoryl trichloride and phosphorothionyl trichloride to a solution of sodium ethyl mercaptide. It was noted that at 120–130° C., triethyl phosphorotetrathioate decomposes to triethyl phosphorotrithioite and sulphur, a reverse of the usual addition reaction of sulphur to

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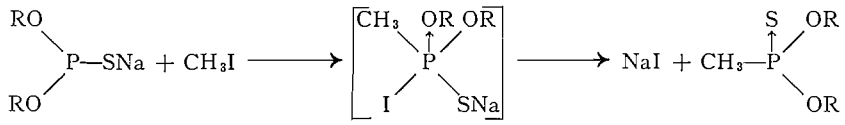
phosphites at these temperatures. This side reaction makes it difficult to obtain a pure sample of triethyl phosphorotetrathioate.

$$(C_2H_5S)_3P(S) \longrightarrow (C_2H_5S)_3P + S$$

OOS-Triethyl phosphorothioate was obtained in low yields by the disproportionation of diethyl phosphorothioic acid, and by refluxing triethyl phosphorothionate with ethyl iodide.

Dialkyl alkylphosphonates were made by the Arbusov rearrangement of trialkyl phosphites with the appropriate iodide (25). Methyl- and ethylphosphonyl dichloride were obtained as described by Kinnear and Perren (24).

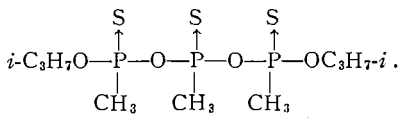
Di-isopropyl methylphosphonothionate can be made by the procedure of Kabachnik *et al.* (23). In our hands, the thiono isomer was the sole product,



so it is improbable that any splitting of RI occurred (as in the Arbusov reaction), followed by readdition to the resulting sodium salt, since if this occurred, the thiolo isomer would be present.

Methylphosphonothionyl dichloride was obtained by the method described by Kinnear and Perren (24) or by the addition of sulphur to methylphosphonous dichloride (3, 17, 31, 35).

Bis(isopropyl methylphosphonothionyl) methylphosphonothionate was obtained during an attempt to make di-isopropyl dimethyldithionopyrophosphonate by an adaptation of the procedure of Toy (37). Because of incomplete fractionation of the starting material from methylphosphonothionyl dichloride, the product actually obtained was



Attempts to produce compounds with authentic P—S—P structures by the following reactions failed.

$$(C_2H_5O)_2PSSH + DCC^* \longrightarrow (C_2H_5O)_2P(S)—S—P(S)(OC_2H_5)_2 .$$

$$(C_2H_5O)_2P(S)SNa + (C_2H_5O)_2P(S)Cl \longrightarrow (C_2H_5O)_2P(S)—S—P(S)(OC_2H_5)_2 + NaCl .$$

$$(C_2H_5O)_2P(S)SNa + (C_2H_5O)_2P(O)Cl \longrightarrow (C_2H_5O)_2P(S)—S—P(O)(OC_2H_5)_2 + NaCl .$$

In all cases there were indications that the crude reaction mixture contained the required product. The compounds decomposed completely when distilled on the falling-film evaporator, although crude thionopyrophosphates could be successfully distilled by this technique. The distilled product was almost pure

**DCC = Dicyclohexylcarbodiimide.*

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OOS-triethyl phosphorodithioate. The constituents of the undistillable residue were not investigated further, but there was no infrared evidence for a P—S—P bond.

EXPERIMENTAL

Sodium analyses were carried out using a Beckman DU Spectrophotometer with flame attachment.

Dialkyl Hydrogen Phosphonates and Dialkylphosphorochloridates

The appropriate alcohol (1.5 mole) was mixed with dry benzene (150 ml.) and chilled to 5° C. Phosphorus trichloride (0.5 mole) in an equal volume of benzene was added dropwise with the temperature being kept below 10° C. The hydrogen chloride, alkyl chloride, and benzene were distilled off at room temperature if it was desired to isolate the hydrogen phosphonate, otherwise sulphuryl chloride (0.5 mole) in an equal volume of benzene was immediately added to the reaction mixture, the temperature being maintained below 10° C. Gases and solvents were then stripped off at room temperature, and the residual product used directly. The refractive indices cited in Table II were obtained on this crude product.

TABLE II
$(RO)_2P(O)X$

	X = H			X = Cl		
R	Yield, %	n_D^{25}	n_D^{20} Lit.*	Yield, %	n_D^{25}	n_D^{25} Lit. (13)
CH_3	87	1.4018	1.4036 (5)	100	1.4107	1.4107
C_2H_5	83	1.4112	1.4080 (5)	95	1.4160	1.4162
n-C_3H_7	93	1.4155	1.4163 (25) (29)	96	1.4159	1.4159
i-C_3H_7	87	1.4082	1.4070 (25) (29)	100	1.4256	1.4236
n-C_4H_9	86	1.4213	1.4230 (25) (29)	94	1.4291	1.4289

**Only one value is cited for each compound, but other values summarized by Kosolapoff (25) show considerable variation for the same compound (from 0.002 to 0.007).*

Diethyl Phosphorothioic Acid and OOS-Triethyl Phosphorothioate

Diethyl hydrogen phosphate (0.5 mole) was dissolved in dry ether (120 ml.) and mixed with sulphur (0.5 mole). Triethylamine (0.5 mole) dissolved in an equal volume of dry ether was added dropwise. After the addition was complete, the reaction mixture was heated until all of the sulphur was dissolved. It was then filtered and treated with an excess of concentrated hydrochloric acid. The ether layer was separated, and the aqueous layer extracted with ether. The combined extracts were evaporated, yielding 85.9 gm. of crude material (100%); n_D^{25} 1.4678; n_D^{25} 1.4682 (36). Some of this was distilled from a Späth bulb in an air bath at pressures ranging from 6 to 60 μ. The distilled material showed a new band appearing in the potassium bromide region of the infrared spectrum, and the spectrum also indicated some loss of sulphur.

Another preparation (107 gm.) of this compound was distilled at temperatures ranging from 80° to 120° C. at varying pressures. The distillate (29.5 gm.)

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proved to be *OOS*-triethyl phosphorothioate. Further distillation was not possible owing to excessive decomposition. The residue was taken up in water, extracted with ether to remove neutral and extractable acidic products, and the aqueous layer concentrated. An oil was obtained which showed the same infrared spectrum as a sample of $C_2H_5O—P(S)(OH)_2$ obtained by hydrolysis of $C_2H_5O—P(S)Cl_2$.

The *OOS*-triethyl phosphorothioate was refractionated with a Podbielniak whirling band column; b.p. (4.5 mm.) 81.5° C.; n_D^{25} 1.4560. Lit. b.p. (1 mm.) 75° C.; n_D^{25} 1.4552 (20). *OOS*-Triethyl phosphorothioate was also prepared in 62% yield by refluxing triethyl phosphorothionate (19.5 gm.) with an equal weight of ethyl iodide for 24 hr. Fractionation with a Widmer column yielded ethyl iodide, unchanged triethyl phosphorothionate and *OOS*-triethyl phosphorothioate; b.p. (5 mm.) 83° C.; n_D^{25} 1.4553. This latter method of isomerization seems to be a general reaction of phosphorothioates.

Dialkyl Phosphorochloridothionates and Alkyl Phosphorodichloridothionates

Ethanol (48.2 gm.) was added slowly to phosphorothionyl trichloride (169.4 gm.) at 10° C. Stirring was continued for five hours during which period the temperature was raised slowly to 47° C. The resulting crude $C_2H_5O—P(S)Cl_2$ was treated with sodium hydroxide (40 gm.) in ethanol (320 ml.) while the temperature was maintained at 15° C. The reaction mixture was cooled overnight, filtered from sodium chloride, concentrated *in vacuo*, and distilled. Yield 50 gm. (38%); b.p. (1.5 mm.) 58° C.; n_D^{25} 1.4725. Lit. b.p. (3 mm.) 62° C.; n_D^{25} 1.4684 (15). This product contained considerable ethyl phosphorodichloridothionate.

This method was also used for preparing the dimethyl analogue. Ethyl phosphorodichloridothionate and methyl phosphorodichloridothionate were made in a similar fashion, using 200 ml. of petroleum ether or benzene as a solvent and bubbling a stream of nitrogen through the reaction mixture to sweep out hydrogen chloride. The methyl phosphorodichloridothionate was particularly difficult to free from phosphorothionyl trichloride.

CH_3OPSCl_2: Yield 70%; b.p. (11 mm.) 45° C.; n_D^{25} 1.5124. Lit. b.p. (40 mm.) 70° C. (30). Found: C, 6.92, 7.46; H, 1.78, 1.84. Calculated: C, 7.28; H, 1.83. $C_2H_5OPSCl_2$: Yield 59%; b.p. (14 mm.) 57–59° C.; n_D^{25} 1.5026. Lit. b.p. (20 mm.) 68° C. (30), 52° C. (9). Found: C, 13.58; H, 3.02. Calculated: C, 13.42; H, 2.82.

This method is not as easy to apply to higher alcohols, because of the relative insolubility of sodium and potassium hydroxides in these alcohols.

Dialkyl Phosphorodithioic Acids

These compounds were prepared in the manner described by Fletcher *et al.* (16). After the alcohol addition, the benzene was removed, and the crude material added to sodium carbonate solution (85 gm. in 1200 ml. water) at room temperature in a nitrogen atmosphere. The solution was extracted with ether, and the ether extract dried and concentrated. This yielded on fractionation (where R = Et) *OOS*-triethyl phosphorodithioate (also obtained as described below) and *SS*-bis(diethyl phosphorothionyl)-*O*-ethyl phosphoro-

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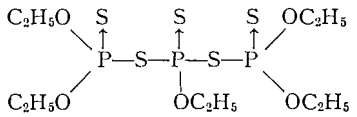
thionate (I), m.p. 47° C. (from petroleum ether). Found: C, 24.64, 24.70; H, 5.37, 5.32. Calc. for $C_{10}H_{25}P_3S_5O_5$: C, 25.10; H, 5.27.



I

The aqueous fraction was acidified, extracted with ether, and the extracts were dried and concentrated. The residue was distilled under reduced pressure.

Compound	Yield, %	B.p.	n_D	Lit. n_D^{20} (22)
$(CH_3O)_2PSSH$	80 (crude)	70.5° C. (5 mm.)	1.5328 (25°)	1.5343
	32 (pure)		1.5346 (20°)	
$(C_2H_5O)_2PSSH$	53	65° C. (0.75 mm.)	1.5096 (25°)	1.5076

Sodium Dialkyl Phosphates

(1) The appropriate trialkyl phosphate (12) (1 mole) was mixed with sodium hydroxide (1 mole) in 80% EtOH (500 ml.) and allowed to stand three to four hours. The alcohol and water were removed *in vacuo*, benzene (150 ml.) was added, and the suspension was evaporated to dryness. The salt so obtained was washed with ether and stored in a desiccator. Yields were quantitative.

$(CH_3O)_2POONa$.—Found: Na, 15.7. Calc. for $C_2H_6PO_4Na$: Na, 15.52.

$(C_2H_5O)_2POONa$.—Found: Na, 13.0. Calc. for $C_4H_{10}PO_4Na$: Na, 13.06.

(2) The appropriate dialkyl phosphorochloridate was hydrolyzed in hot water until all had dissolved. It was then allowed to stand for an additional two hours. The aqueous solution was concentrated until no odor of hydrogen chloride remained, the residue brought to pH 9 with 0.1 *N* sodium hydroxide, and the resulting solution evaporated to dryness. Benzene was then added, the suspension re-evaporated to dryness, the salt washed with ether, and stored in a desiccator. Products obtained in this way were very hygroscopic and tended to have high sodium analyses, probably due to sodium chloride. The *n*-propyl, isopropyl, and *n*-butyl salts were prepared by this method. Diethyl hydrogen phosphate was prepared as described above omitting the neutralization step.

$(n\text{-}C_3H_7O)_2$ POONa.—Found: Na, 11.51. Calc. for $C_6H_{14}PO_4Na$: Na, 11.3.

$(i\text{-}C_3H_7O)_2$ POONa.—Found: Na, 11.97. Calc. for $C_6H_{14}PO_4Na$: Na, 11.3.

$(n\text{-}C_4H_9O)_2$ POONa.—Found: Na, 10.59. Calc. for $C_8H_{18}PO_4Na$: Na, 9.93.

Diethyl Phosphorothiocyanidate

Diethyl phosphorochloridate (21 gm.) was dripped into a stirred solution of potassium thiocyanate (11.8 gm.) in methylethylketone (80 ml.). The solution gradually turned red, and a precipitate of potassium chloride developed. The mixture was allowed to stand overnight and was filtered through

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sintered glass. It was then distilled at reduced pressure, b.p. (0.6 mm.) 77° C. Yield 9.1 gm. (42%); LD_{50} (mice, intraperitoneal (IP)) *ca.* 4 mgm./kgm.; λ_{max} 245 mμ, perhaps by decomposition since ϵ_{max} increases rapidly with time. Lit. b.p. (0.5 mm.) 76–78° C. (38).

Tetraalkyl Monothionopyrophosphates

(1) A well-stirred solution of diethyl hydrogen phosphonate (40 gm., 0.29 mole) in pyridine (23 gm., 0.25 mole) was cooled to 0° C., and sulphur monochloride (19.6 gm., 0.145 mole) was added over a period of three hours, while the temperature was maintained below 5° C. It was necessary to add an additional 30 ml. of pyridine to keep the reaction mixture fluid. The mixture was refrigerated overnight, filtered, and concentrated under reduced pressure. Pyridine hydrochloride separated during the distillation, and although the crude material was highly toxic, the distillation products (b.p. (1 mm.) 85–90° C., total 22 gm.) were practically non-toxic. Refractive indices (n_D^{25}) of fractions ranged from 1.4422 to 1.4525 [$(C_2H_5O)_3PS$, n_D^{20} 1.4480 (4), $(C_2H_5O)_2POSC_2H_5$, n_D^{25} 1.4552 (20)] and the spectra suggested mixtures of $(C_2H_5O)_2POS(C_2H_5)$ and $(C_2H_5O)_3PS$.

(2) Dry pyridine (45 ml.) was placed in a flask equipped with stirrer, dropping funnel, and calcium chloride and gas inlet tubes. Diethyl phosphorochloridate (25 gm.) was added dropwise while the temperature was maintained below 15° C. Hydrogen sulphide was then bubbled in for 90 min. The mixture was then filtered from pyridine hydrochloride and the precipitate washed twice with benzene (50 ml.). The filtrate was evaporated to dryness, redissolved in benzene (75 ml.), and the solution successively washed with 2% hydrochloric acid, water, 5% sodium bicarbonate, and water (20 ml. of each). The benzene solution was dried with sodium sulphate and the benzene removed at reduced pressure. The residue was then distilled, b.p. (0.8 mm.) 129–134° C. Found: C, 30.97, 31.36; H, 7.00, 7.19. Calc. for $C_8H_{20}P_2O_6S$: C, 31.37; H, 6.58.

A similar procedure gave tetrapropyl monothionopyrophosphate as a very pale yellow liquid, b.p. (0.045 mm.) 125–127° C. Yield 60%. Found: C, 40.13, 40.46; H, 7.78, 8.11; P, 17.73, 17.34. Calc. for $C_{12}H_{28}O_6P_2S$: C, 39.76; H, 7.79; P, 17.10.

This procedure failed for tetramethyl monothionopyrophosphate. When distillation was attempted, either with or without the washing procedure, it gave irreproducible results for all other ester groups.

(3) The appropriate dialkyl hydrogen phosphonate (0.25 mole) was dissolved in anhydrous ether (90 ml.) and mixed with sulphur (8.0 gm., 0.25 mole). Triethylamine (20.3 gm., 0.25 mole) dissolved in ether (30 ml.) was then added dropwise at such a rate as to maintain the ether at reflux. After all the sulphur was dissolved, the appropriate dialkyl phosphorochloridate (0.25 mole) was added dropwise. The mixture was filtered from triethylamine hydrochloride, and the ether removed *in vacuo*. The residue was used as such, or purified either by paper chromatography (11) or by passing a chloroform solution of the compound through a short alumina column employing five to seven times more alumina than compound. It was then eluted with chloroform. The recovered material was further purified by conventional distillation, or

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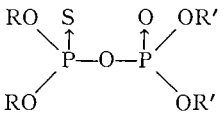
distillation using a falling-film evaporator. Crude yields were excellent, but compounds containing methyl groups resisted all purification attempts. The results are listed in Table III.

TABLE III



R	R′	Yield (crude), %	n_D^{25}	n_D^{25} Lit. (14)
CH_3	CH_3	85	1.4540	1.4519
CH_3	C_2H_5	66	1.4439	1.4499
C_2H_5	CH_3	72	1.4513	
C_2H_5	C_2H_5	100	1.4479	1.4490
n-C_3H_7	*n*-C_3H_7	94 (from PCl_3)	1.4399	1.4363
i-C_3H_7	*i*-C_3H_7	72 (from PCl_3)	1.4370	1.4370
n-C_4H_9	*n*-C_4H_9	91	1.4522	1.4517

(4) Sodium diethyl phosphate (8.8 gm.) was added to diethyl phosphorochloridothionate (9.42 gm.), followed by pyridine (five drops). The reaction mixture was then stirred magnetically for 17.5 hr. During this time the original gelatinous suspension gradually gave way to a fluid suspension of sodium chloride. The sodium chloride precipitate was filtered off, and the residual liquid distilled rapidly in a Späth bulb, the temperature being kept below 75° C. The initial fraction was mainly unreacted phosphorochloridothionate, but when the pressure was lowered to 7μ, the thiopyrophosphate distilled. Yield 7.8 gm. (80%); LD_{50} *ca.* 1 mgm./kgm. (mice, IP). Found: C, 31.52, 31.56; H, 6.71, 6.98; n_D^{25} 1.4491. Calc. for $C_8H_{20}O_6P_2S$: C, 31.37; H, 6.58. Lit. n_D^{25} 1.4490 (14).

A paper chromatographic analysis, however, separated this into tetraethyl pyrophosphate (25%), tetraethyl monothionopyrophosphate (62%), and tetraethyl dithionopyrophosphate (13%).

Tetraethyl monothionopyrophosphate.—Found: C, 31.55; H, 6.65; n_D^{25} 1.4483. Calc. for $C_8H_{20}O_6P_2S$: C, 31.37; H, 6.58. Lit. n_D^{25} 1.4490 (14).

Tetraethyl dithionopyrophosphate.—Found: C, 30.20; H, 6.28; n_D^{25} 1.4758. Calc. for $C_8H_{20}O_5P_2S_2$: C, 29.81; H, 6.25. Lit. n_D^{25} 1.4760 (38).

Although the preparation of all other members of the series was investigated by this method, only the ethyl compound gave satisfactory results. The proportion of dithiono compound produced was greater for the larger alkyl groups owing to the increased hygroscopicity of the corresponding salts, and the difficulty of completely removing water during the preparation.

(5) Dicyclohexylcarbodiimide (658 mgm.) was dissolved in anhydrous ether (20 ml.) and diethyl phosphorothioic acid (1.070 gm.) added. There was no visible reaction. The mixture was allowed to remain 72 hr. at room temperature, the ether was then concentrated to a small volume, and petroleum ether added to induce crystallization. Dicyclohexyl thiourea (402 mgm.) separated. Repetition of the crystallization process yielded an additional 481 mgm. of the

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thiourea. The filtrates were evaporated, giving two fractions; the first (possibly overheated) was non-toxic, with n_D^{25} 1.4910. The second had an LD_{50} (mice, IP) of *ca.* 1.8 mgm./kgm. and n_D^{25} 1.4492. Found: C, 30.17, 30.17; H, 7.02, 6.65. Calc. for $C_8H_{20}O_6P_2S$: C, 31.37; H, 6.55. The analysis, infrared spectrum, and refractive index indicate that the latter product contains probably 50% tetraethyl monothionopyrophosphate with some *OOS*-triethyl phosphorothioate and some unchanged diethyl phosphorothioic acid. This experiment was repeated using larger quantities but there was no apparent reaction in three months at room temperature.

Dialkyl Hydrogen Phosphonothioates and OOS-Trimethyl Phosphorodithioate

P_4S_7 (0.5 mole) was added gradually to the appropriate alcohol (6 mole) with heating. The reaction was refluxed for 24 hr., filtered from sulphur, and excess alcohol removed *in vacuo*. The products were then fractionally distilled with a Widmer column, and small portions were further fractionated with a Podbielniak whirling band column. Methanol yielded $(CH_3O)_2P(S)H$ (0.24 mole); b.p. (10 mm.) 24.3° C.; n_D^{25} 1.4772. Lit. n_D^{20} 1.4768 (21). $(CH_3O)_2P(S)SCH_3$ (0.86 mole) was also obtained; b.p. (5 mm.) 64° C.; n_D^{25} 1.5244. Lit. n_D^{20} 1.5292 (21). Found: C, 20.93, 21.27; H, 5.60, 5.74. Calc. for $C_3H_9PO_2S_2$: C, 20.92; H, 5.27.

Ethanol yielded $(C_2H_5O)_2P(S)H$ (0.29 mole); b.p. (5 mm.) 49.2° C.; n_D^{25} 1.4589. Lit. n_D^{20} 1.4597 (21).

OOS-Trimethyl phosphorodithioate was also produced by the reaction of methanol with P_4S_{10}.

SSS-Triethyl Phosphorotrithioate and Triethyl Phosphorotetrathioate

Sodium metal (6.9 gm., 0.3 mole) was powdered in hot toluene (75 ml.) and ethyl mercaptan (18.6 gm., 0.3 mole) added. The mixture was heated until all the sodium had reacted, a slight excess of mercaptan being added if necessary. The mixture was cooled and phosphoryl trichloride (15.35 gm., 0.1 mole) added slowly, followed by heating to 50° C. for 30 min. The resultant suspension was washed thrice with water and the toluene layer dried and evaporated. The residue was distilled in a falling-film evaporator, and a small portion purified by fractionation in the Podbielniak still. Yield 17.5 gm. (75%); b.p. (3 mm.) 124.5° C.; n_D^{25} 1.5664. Found: C, 31.19; H, 6.95. Calc. for $C_6H_{15}POS_3$: C, 31.28; H, 6.56.

Similarly, using phosphorothionyl trichloride (16.95 gm., 0.1 mole), triethyl phosphorotetrathioate (14.9 gm., 61%) was obtained; n_D^{25} 1.6083. Lit. n_D^{25} 1.6201 (10). Analysis of this material gave C, 30.15; H, 6.42. Calc. for $C_6H_{15}PS_4$: C, 29.25; H, 6.14. Distillation in the Podbielniak gave $(C_2H_5S)_3P$ (identified by infrared spectrum, qualitative tests, and n_D^{25} = 1.5670). Lit. n_D^{25} 1.5689 (27). A residue of sulphur remained in the flask.

Di(Isopropyl Methylphosphonothionyl) Methylphosphonothioate

Isopropyl methylphosphonochloridothionate containing some methylphosphonothionyl dichloride (17.1 gm.) was dissolved in benzene (25 ml.). To this a mixture of pyridine (30 ml.) and water (1.2 ml.) was added dropwise with stirring. A heavy precipitate of pyridine hydrochloride formed. The

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mixture was cooled in ice, filtered, recooled, and refiltered. The solvents were stripped off. The residue was redissolved in benzene (50 ml.) and washed twice with water (25 ml.). The benzene fraction was concentrated and vacuum-distilled. Yield 2.4 gm.; b.p. (1 mm.) 170° C.; n_D^{25} 1.5244. Found: C, 27.02, 27.11; H, 6.07, 5.86; P, 23.99, 24.08%. Calculated for $C_9H_{23}O_4P_3S_3$: C, 28.11; H, 6.03; P, 24.17.

Attempts to Produce a P—S—P Compound

(1) Dicyclohexylcarbodiimide (459 mgm.) was dissolved in anhydrous ether (10 ml.) and diethyl phosphorodithioic acid (890 mgm.) was added. A slight increase in temperature was noted. The ether was evaporated and the residue triturated with petroleum ether yielding amorphous dicyclohexyl thiourea (352 mgm.). Recrystallization from alcohol gave the pure thiourea; m.p. 181° C. (Kofler Block). Evaporation of the petroleum ether gave a pale yellow oil (598 mgm., 75%); n_D^{25} = 1.5142. Infrared and elemental analyses indicated that this was probably a mixture of unchanged starting material and P—S—P compound.

(2) Diethylphosphorodithioic acid (9.3 gm.) in chloroform (20 ml.) with triethylamine (5 gm.) was treated with diethyl phosphorochloridothionate (9.4 gm.). The reaction mixture was refluxed for six hours, but no precipitation was noted. Evaporation of the chloroform gave a slurry which was filtered. The crude material appeared to contain some P—S—P compound (infrared spectrum) but when distilled using a falling-film evaporator, yielded only *OOS*-triethyl phosphorodithioate. A portion of this was fractionated in the Podbielniak yielding $(C_2H_5O)_2P(S)SC_2H_5$; b.p. (4.5 mm.) 87° C.; n_D^{25} 1.5024. Lit. n_D^{20} 1.5013 (21).

Repetition of the above experiment using diethyl phosphorochloridate in place of the thiono compound gave the same results. $(C_2H_5O)_2P(S)SC_2H_5$ was isolated and purified as above.

RÉSUMÉ

Nous avons étudié plusieurs méthodes pour la synthèse des esters de l'acide thiopyrophosphorique. Une de ces méthodes est très rapide et donne de très bons rendements. La purification de ces composés est très difficile, car ils sont instables en présence de faibles quantités d'acide ou d'alcali, et même de sels inorganiques à des températures plus élevées que 70° C. Toutes les méthodes étudiées donnent exclusivement l'isomère thiono, et nulle trace de l'isomère au groupement P—S—P a été identifiée. Les données toxicologiques ne confirment pas les résultats de Fiszer *et al.*, car aucun de ces composés fut plus toxique en injection intraveineuse que le pyrophosphate tétraéthylique. La synthèse de quelques autres composés pour l'étude de spectres infrarouges est aussi décrite.

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INFRARED SPECTRUM OF SOLID SULPHUR DIOXIDE

By Paul A. Giguère and M. Falk[1]

In connection with a spectroscopic study of the molecular nature of sulphurous acid we needed data on the absorption of solid sulphur dioxide in the infrared. As it could not be found in the literature* we have measured this spectrum at liquid air temperature over the range 2–25 μ. The samples were prepared by condensing small amounts of the gas from a commercial cylinder, without further purification, onto a sodium chloride or silver chloride plate mounted in a conventional low temperature cell. Clear, non-scattering films were thus obtained with thickness estimated of the order of 1 to 10 microns; the thicker films appeared translucent. The spectra were recorded with a Perkin–Elmer instrument, Model 12-C, using alternately prisms of LiF, NaCl, KBr, or CsBr.

TABLE I

Frequencies of infrared absorption bands in solid sulphur dioxide at −180° C.

Gas,* cm.$^{-1}$	Liquid,† cm.$^{-1}$	Solid, cm.$^{-1}$	Solid–gas shift, cm.$^{-1}$	Band width, cm.$^{-1}$	Assignment
		517		2	$\nu_2-\nu_L$ (?)
		521			$\nu_2(S^{34}O_2)$ (?)
518	524.5	528	+10	25	ν_2
		535			
		1121		3	$\nu_1-\nu_L$
		1140		2	$\nu_1(S^{34}O_2)$
1151	1144.3	1144	−7	10	ν_1
		1303			$\nu_3(S^{34}O_2)$
1362	1336.0	1310 1322	−46	35	ν_3
		1334			$\nu_3+\nu_L$ (?)
2296		2287		2	$2\nu_1$
		2432		2	$\nu_1+\nu_3(S^{34}O_2)$
2500		2455		4	$\nu_1+\nu_3$

*From Ref. 6.
†Raman spectrum: Ref. 1.

The results are listed in Table I and tracings of the regions of the three fundamentals are shown in Fig. 1. Of these three only ν_1, the symmetric stretching, gives rise to a sharp band (1144 cm.$^{-1}$). The asymmetric stretching band ν_3 was resolved, in thin samples, into two equally intense components

[1]*Holder of a Cominco Fellowship.*

*Note added in proof: *Shortly after our manuscript was submitted for publication we came across a note by R. N. Wiener and E. R. Nixon (J. Chem. Phys. 25: 175. 1956) in which these authors report eight bands in the infrared spectrum of solid sulphur dioxide. Their interpretation differs from ours mainly in that they did not consider the possibility of assigning some of the weak bands to the isotopic molecule* $S^{34}O_2$.

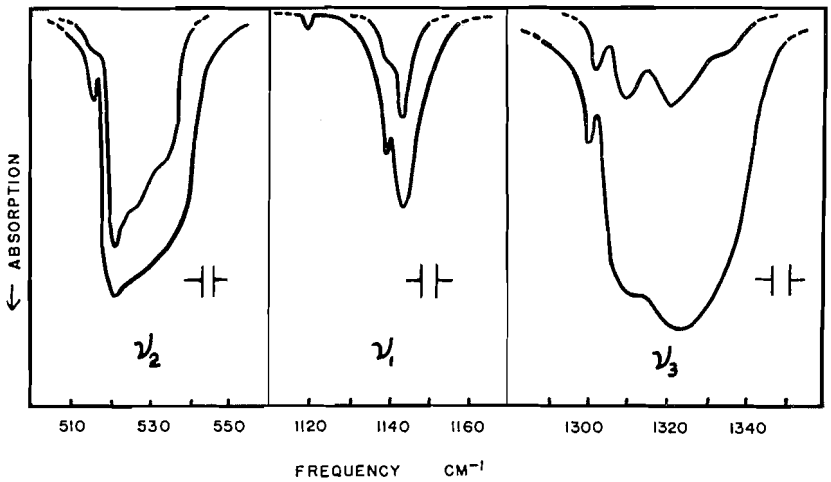

FIG. 1. Infrared spectrum of solid sulphur dioxide at −180° C. in the regions of the three fundamentals.

split by about 12 cm.$^{-1}$. Such splittings are common in the molecular spectra of crystalline solids; they have been explained theoretically by correlation with the structure of the crystals (2, 3, 7). A recent X-ray study of the single crystal of sulphur dioxide has confirmed that the unit cell is orthorhombic with four molecules and a probable space group *Aba* (5). As for the broad, asymmetric band due to the bending mode ν_2, it could not be resolved clearly even in the thinnest films and with the maximum resolution available. At best, vague indications of flat maxima appeared at 528 and 535 cm.$^{-1}$ in addition to the stronger peak at 521 cm.$^{-1}$. We are inclined to consider the latter as arising from superposition of the ν_2 band of the isotopic molecule $S^{34}O_2$, of which the natural concentration is 4.2%. In support of this view is the fact that the peak lies some 7 cm.$^{-1}$ on the low-frequency side of the center of the broad band, and the calculated isotope shift for that mode is exactly 7 cm.$^{-1}$ (6). These isotopic bands have not been observed in the gas because of overlapping by the rotational structure of the main bands. The other two fundamental bands also show weak satellites assignable to the isotopic molecule: at 1140 cm.$^{-1}$ for ν_1 (observed shift about 4 cm.$^{-1}$; calculated, 2.5 cm.$^{-1}$; intensity about 1/20 of the main band), and at 1303 cm.$^{-1}$ for ν_3 (shifted some 13 cm.$^{-1}$ from the center of the doublet; calculated shift, 17 cm.$^{-1}$). It is suspected that the latter band is of complex origin because its intensity decreased only slightly in thinner films while its apparent frequency increased somewhat (from 1301 to 1304 cm.$^{-1}$). None of the isotopic bands showed any indication of structure as already found in the case of CO_2 and HCl (4).

In contrast with the spectrum of the gas, where over a dozen combination and overtone bands have been observed (6), only two could be detected even in the thickest samples of solid sulphur dioxide. The very weak band at 2287 cm.$^{-1}$ can be assigned unambiguously to $2\nu_1$; as in the case of the gas the anharmonicity is quite small. The stronger band at 2455 cm.$^{-1}$, which is due to combination of the two stretching modes, has a weak satellite at 2432 cm.$^{-1}$

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with the right intensity and frequency shift for the isotopic molecule $S^{34}O_2$. The remaining weak maxima at 517 cm.$^{-1}$ and 1121 cm.$^{-1}$ on the low-frequency side of ν_1 and ν_2 may be assigned to difference combinations with lattice frequencies ν_L of the order of 11 and 23 cm.$^{-1}$ respectively, which seem reasonable for hindered rotations or translations of SO_2 molecules in the crystal. On the other hand, considering the uncertainty about the center of the ν_2 fundamental, it must be noted that the shoulder at 517 cm.$^{-1}$ is also of the right intensity for the bending mode of the isotopic molecule. Likewise the flat maximum at 1334 cm.$^{-1}$ is tentatively assigned to a combination with a lattice mode.

As for the solid–gas frequency shifts, they are in the direction to be expected normally for bending and stretching modes; their magnitude is obviously much less than for hydrogen bonded crystals but still fairly large (especially for ν_3) in keeping with the high polarity of the SO_2 molecule (1.62 debyes). The frequency of the fundamentals in the liquid state, as found in the Raman spectrum (1), is intermediate between those of the gas and the solid. Outside the bands reported in Table I the absorption of even the thickest films was always low and constant; there were no indications of reflection peaks (4) nor of absorption from impurities.

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ALCOHOLIC HEXANITRATO AMMONIUM CERATE AS A QUANTITATIVE OXIDANT FOR ORGANIC SUBSTANCES

BY D. G. M. DIAPER AND F. R. RICHARDSON

A qualitative test for the alcoholic hydroxyl group using certain complex cerate anions was first proposed by Duke and Smith (1) and has been used with success in student courses in the identification of organic unknowns in many schools (2). Duke and Smith note that the orange color produced by interaction of the cerate and alcohol is bleached by easily oxidized materials, and we have now found it possible, in favorable cases, to make quantitative use of this bleaching reaction in the determination of such materials in alcoholic solution.

REAGENTS

Hexanitrato ammonium cerate was employed in aqueous solution, without the addition of nitric acid, in concentrations ranging from 0.1 to 0.3 molar. This solution should be freshly prepared each day. It should not be heated, for

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hydrolysis to basic cerium compounds easily occurs, and such substances interfere with the analysis by causing turbidity when mixed with non-aqueous solutions.

Methanol and ethanol were used interchangeably as the principal solvents. It was found that benzene and ether did not interfere with the development or bleaching of the reagent in concentrations up to 30%.

APPLICATION

For successful quantitative use of the oxidant it is desirable that the substance under test should decolorize it instantly and completely. The following substances were found suitable: anethole, hydroxylamine, oxalic acid, and the oximes of *cyclo*hexanone, *cyclo*heptanone, heptaldehyde, and butyraldehyde. Vanillin decolorized the reagent, but gave a yellow end product which obscured the volumetric end point. Using a spot-plate technique, suitable substances may be detected in quantities as small as 10 μgm.

VOLUMETRIC TECHNIQUE

The substance, dissolved in methanol, may be titrated by the addition of the aqueous cerate from a burette. It was found advisable to add aqueous nitric acid, to a final concentration of 0.1–0.2 *N*, to catalyze the oxidation. At the end point, excess of cerate causes a yellow-orange color to appear and no indicator is required. Diphenylamine and ferrous phenanthroline sulphate could not be used in the alcoholic solutions employed. Fading of the end point color, presumably due to attack of the solvent by the oxidizing agent, was troublesome. Strong light, especially direct sunlight or the light from overhead fluorescent fixtures, promotes fading. Excessive amounts of acid have the same effect.

An end point was obtained when three equivalents of cerate had been added to each of the oximes mentioned. Anethole consumed 1.5 equivalents of oxidant and oxalic acid consumed two equivalents.

COLORIMETRIC TECHNIQUE

A 0.01 molar solution of cerate in methanol has a strong orange-red color which persists for many hours if the solution is kept in the dark. Light or heat or acid promote fading, but attempts to diminish the natural acidity of the solution were unsuccessful, as all buffer systems tried produced turbidity. Addition of progressive amounts of the organic substances mentioned above diminished the color through yellow to colorless. Examination of the solutions in a Beckmann spectrophotometer showed that there was no absorption peak in the visible range, but general absorption increasing towards the shorter wavelengths. A Klett-Summerson colorimeter with the appropriate green filter proved suitable for these colorimetric determinations, and for each substance a range of standards was set up. An unknown was determined by interpolation. Quantities up to 10 mgm. were thus determined with a precision of ± 0.1 mgm. in 10 ml. of solution.

Because the alcohol–cerate color does not develop instantaneously, and

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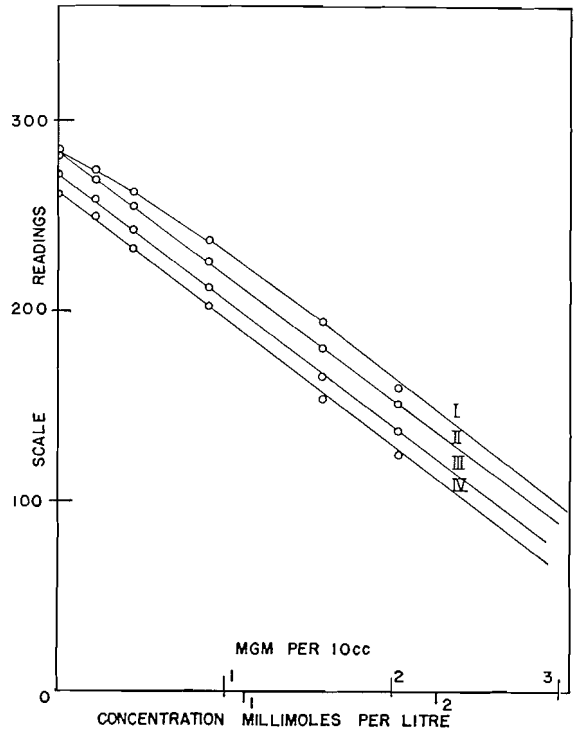

FIG. 1. Plot of colorimeter readings versus concentration for *cyclo*hexanone oxime in methanolic hexanitrato ammonium cerate.

because it slowly fades, the solutions should stand, in the dark, for at least 15 to 20 min. after mixing. This is illustrated in the family of curves of Fig. 1 in which colorimeter readings are plotted against concentration for a series of methanolic solutions of *cyclo*hexanone oxime each of which was initially mixed with 1 ml. of 0.1 molar aqueous hexanitrato ammonium cerate. Curves I, II, III, and IV represent the same samples 5 min., 15 min., 30 min., and 60 min. after mixing. After the initial slow development of the color, the plots are linear and, as the colorimeter scale is logarithmic, this would indicate that the system obeys the Beer-Lambert Law.

Further work is planned on the scope of the reaction and the chemical nature of the products.

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